Magnetization of $S = 1$ antiferromagnetic Heisenberg chains

Shoji Yamamoto
Department of Physics, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Seiji Miyashita
Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606, Japan
(Received 31 August 1994)

Full magnetization curves of $S = 1$ antiferromagnetic Heisenberg chains with periodic and open boundaries are investigated by a quantum Monte Carlo method. The boundary condition has a significant effect on the magnetization process especially in the field range where the Zeeman energy is less than the Haldane gap. The magnetization of the periodic chain in the range is strongly suppressed at low temperatures because the ground state is nonmagnetic. On the other hand, the magnetic ground states of the open chain bring about finite magnetization. The difference between both the magnetization curves is also investigated in detail by subtracting the magnetization of the periodic chain with L spins from one of the open chains with $L + 1$ spins. It agrees well with the double of the Brillouin function for $S = \frac{1}{2}$, rather than the Brillouin function for $S = 1$.

I. INTRODUCTION

Antiferromagnetic quantum spin chains have been of great interest in recent years due to the Haldane conjecture.[1] Following this conjecture, the linear-chain Heisenberg antiferromagnet described by the Hamiltonian

$$\mathcal{H} = J \sum_i \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1} \tag{1.1}$$

should exhibit an energy gap between the ground state and the first excited state for integer spin cases, while it has a gapless excitation spectrum for half-odd-integer spin cases. In the case of $S = 1$, the existence of the gap ΔE has been confirmed by various numerical methods, such as an exact diagonalization method,[2] quantum Monte Carlo methods,[3] a quantum transfer matrix method,[4] and a density-matrix renormalization group method,[5] and the estimation $\Delta E \simeq 0.41J$ now seems to be widely accepted.

On the other hand, extensive experimental evidence of the Haldane gap has also been shown. In particular, Renard *et al.* have reported that $Ni(C_2H_8N_2)_2NO_2ClO_4$ (NENP) is a prototype of the $S = 1$ linear-chain Heisenberg antiferromagnet.[6] High-field magnetization measurements[7] for NENP are one of the most successful experiments in demonstrating the Haldane gap, where a transition from the nonmagnetic to the magnetic state has been observed at a finite magnetic field. These pioneering experiments have stimulated not only experimentalists but also theoreticians to study properties of the so-called Haldane antiferromagnet in a magnetic field. So far calculations of the magnetization curves have been performed for the model (1.1) with the periodic boundary condition. Parkinson and Bonner[8] performed numerical diagonalizations and obtained the magnetization process at $T = 0$ as a step function. Hodgson and Parkinson[9] further discussed the form of the magnetization curve in the vicinity of the saturation field employing a Bethe ansatz approach. Sakai and Takahashi[10] applied a finite-size scaling based on conformal field theory to their numerical diagonalization data and derived the $T = 0$ full magnetization curve in the thermodynamic limit. Their numerical study strongly supported the critical behavior of the magnetization at the saturation field suggested by the Bethe ansatz approach.[9] Delica *et al.*[11] calculated the magnetization process at finite temperatures by a quantum transfer matrix method. Although the calculated temperatures ($k_BT/J \geq 0.12$) are not very much less than the corresponding Haldane gap, their results strongly suggest a nonmagnetic ground state separated from the excitation spectrum by a finite energy gap. All these theoretical results explain well the magnetization measurements[7] although the measurements have been performed for *open* chains rather than periodic chains.

Recently, heavily doped Haldane antiferromagnets have been extensively synthesized and impurity effects on the magnetization process[12,13] have been reported. Renard *et al.*[12] carried out magnetization measurements for copper-doped NENP and observed paramagnetic components consisting of $S = 1/2$ moments. More fascinating results have been obtained from magnetization measurements for nonmagnetic impurity zinc-doped samples,[13] where observed paramagnetic components have still been explained well by the double of the Brillouin function for $S = 1/2$ as in the case of copper doping. All these experiments can be regarded as evidence of $S = 1/2$ effective moments induced at chain ends.[14–16]

In such circumstances, it is worth performing a systematic theoretical study on the finite-temperature magnetization process of both periodic and open chains. In the present paper, we carry out quantum Monte Carlo calculations of the magnetization process up to the saturation field for both periodic and open chains in the tempera-

ture range $k_BT/J \geq 0.10$. The obtained results support the edge-state picture proposed for the Affleck-Kennedy-Lieb-Tasaki (AKLT) valence-bond-solid model.[14] In Sec. II we introduce the model Hamiltonian and briefly describe the calculation procedure. Results are presented in Sec. III. Section IV is devoted to summary and discussion.

II. MODEL AND METHOD

We treat an $S = 1$ linear-chain Heisenberg antiferromagnet in a uniform magnetic field described by the Hamiltonian

$$\mathcal{H} = J\sum_{i}^{L} \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1} - H\sum_{i}^{L} S_i^z , \tag{2.1}$$

where $\boldsymbol{S}_{L+1} = \boldsymbol{S}_1$ for the periodic chain. Here we have taken $L = 36$, namely, the calculations have been carried out for the periodic chain with 36 spins and for the open chain with 37 spins.

The Monte Carlo method used is based on the Suzuki-Trotter decomposition[17] of checkerboard type.[18] As has been explained in Ref. 19, the transformed two-dimensional Ising checkerboard in a magnetic field is slightly modified in accordance with the boundary condition.

Although the Trotter number N should, in principle, be taken to be as large as possible, we have used sets of smaller Trotter numbers than in the case without a field.[20] We list in Table I the sets of Trotter numbers used and the maximum Monte Carlo steps performed for each Trotter number at various temperatures. In order to evaluate the magnetization of the system through a Monte Carlo simulation, enough acceptance ratio should be guaranteed for the global flips which let the total magnetization fluctuate. Therefore we cannot successfully use such large Trotter numbers as used in the case without a field. Furthermore, in comparison with thermodynamic calculations in the nonfield case,[20,21] many more Monte Carlo steps are needed to obtain reliable results. The N dependence of the data is extrapolated into the $N \to \infty$ limit. The data precision, which strongly depends on the magnitude of the magnetic field, is between two and one digits for $H/J \lesssim 0.4$ and between three and two digits for $H/J \gtrsim 0.4$.

TABLE I. Sets of the Trotter numbers used (N) and the maximum Monte Carlo steps (MCS) performed for each Trotter number at given temperatures (T).

k_BT/J	N	MCS
0.10	16, 12, 10, 8	5000000 (periodic chain) / 3000000 (open chain)
0.20	12, 8, 6, 4	1000000
0.30	8, 6, 4, 2	700000
0.50	8, 6, 4, 2	500000
1.00	8, 6, 4, 2	500000

III. RESULTS

In this section we show the magnetization $M = \langle \sum_{i=1}^{L} S_i^z \rangle$ as a function of magnetic field H and temperature T, where $\langle \cdots \rangle$ denotes a thermal average of the quantity. For the periodic chain, calculations have been carried out in the temperature range $0.1 \leq k_BT/J \leq 1.0$, while for the open chain, calculations are in the range $0.1 \leq k_BT/J \leq 0.3$. There is no significant difference between the periodic-chain magnetization and the open-chain one in the high-temperature range $k_BT \gtrsim \Delta E \simeq 0.4J$, where the low-lying level structure is not relevant. Although the actual magnetization measurements[7,13] are generally performed at $0.02 \lesssim k_BT/J \lesssim 0.05$, we were not able to obtain, with feasible Monte Carlo steps, reliable magnetization curves for $k_BT/J < 0.1$, where the global flip is hardly accepted, that is, the total magnetization is very hard to fluctuate.

A. High-field properties

We show in Fig. 1 the full magnetization process at various temperatures for the periodic chain (a) and for

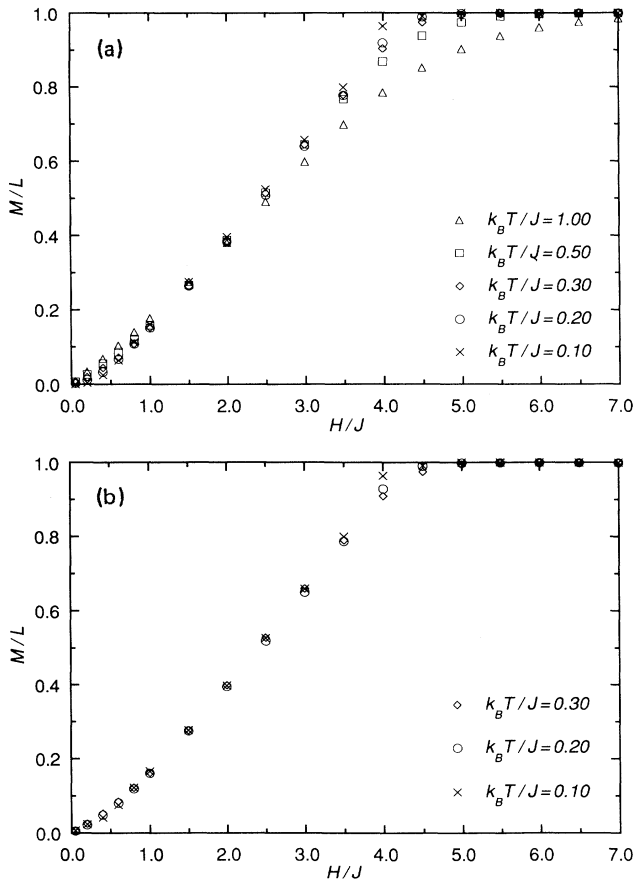

FIG. 1. Full magnetization curves as a function of magnetic field H at various temperatures for the periodic chain (a) and for the open chain (b).

the open chain (b). There is no qualitative difference between the periodic-chain magnetization curves and the open-chain ones in the high-field range. As the temperature goes to zero, the magnetization curves of both the periodic and open chains tend toward the form which agrees well with the exact diagonalization result at the absolute zero temperature.[10] Recently, magnetic saturation has been in fact observed for $(CH_3)_4NNi(NO_2)_3$ (TMNIN).[22]

Let us derive the saturation field.[23] First we consider the periodic chain with L spins. In the subspace with $\sum_{i=1}^{L} S_i^z = L$, the spin configuration is unique and the energy $E_0^{\rm per}(L)$ is given by

$$E_0^{\rm per}(L) = L(J-H)\,. \tag{3.1}$$

In the subspace with $\sum_{i=1}^{L} S_i^z = L-1$, diagonalizing the subspace Hamiltonian, we obtain the ground state energy $E_0^{\rm per}(L-1)$ as

$$E_0^{\rm per}(L-1) = (L-4)J - (L-1)H\,. \tag{3.2}$$

The saturation field $H_{\rm sat}^{\rm per}$ is obtained by equalizing $E_0^{\rm per}(L)$ with $E_0^{\rm per}(L-1)$ and is given by

$$H_{\rm sat}^{\rm per} = 4J\,, \tag{3.3}$$

not depending on the chain length L. Next we consider the open chain with L spins. The energy of the state with a totally ferromagnetic alignment, $E_0^{\rm op}(L)$, is given by

$$E_0^{\rm op}(L) = (L-1)J - LH\,. \tag{3.4}$$

The ground state energy in the subspace with $\sum_{i=1}^{L} S_i^z = L-1$, $E_0^{\rm op}(L-1)$, is obtained as

$$E_0^{\rm op}(L-1) = \left(L-3-2\cos\frac{\pi}{L}\right)J - (L-1)H\,. \tag{3.5}$$

Therefore the saturation field $H_{\rm sat}^{\rm op}$ is dependent on the chain length L and is given by

$$H_{\rm sat}^{\rm op} = 2\left(1+\cos\frac{\pi}{L}\right)J\,. \tag{3.6}$$

The difference of the two saturation fields, which is approximately estimated as $(\pi/L)^2 J$, is now very small and disappears into numerical errors. In fact both the magnetization curves in Fig. 1(a) and Fig. 1(b) show quantitatively almost the same behavior. The temperature dependence of the magnetization curves strongly suggests the anomaly at the saturation field

$$M/L \sim 1 - \frac{2}{\pi}\left(1-\frac{H}{4J}\right)^{1/2}\,, \tag{3.7}$$

which has been predicted by a Bethe ansatz approach.[9]

B. Low-field properties

In order to investigate the low-field magnetization process, we give in Fig. 2 more detailed plots of the magnetization in the range of $H/J \leq 1.0$ for the periodic-chain (a) and for the open chain (b). The periodic-chain data show good agreement with the previous results obtained by a quantum transfer matrix method.[11] In contrast to the high-field behavior, we here find a qualitative difference between the periodic-chain magnetization and the open-chain one, which gets clearer with decrease of temperature.

The temperature dependence of the periodic-chain magnetization is attributed to a nonmagnetic ground state separated from the lowest excited state by a finite energy gap. The gap in a field H is given by[24]

$$\Delta E(H) = \Delta E - H\,, \tag{3.8}$$

which vanishes at $H/J = H_c/J \simeq 0.4$. Below the critical field H_c, the ground state is nonmagnetic and the magnetization monotonically decreases toward zero with decrease of temperature. The magnetization curve at $k_BT/J = 0.10$ shows significant increase at $H/J \simeq 0.3$.

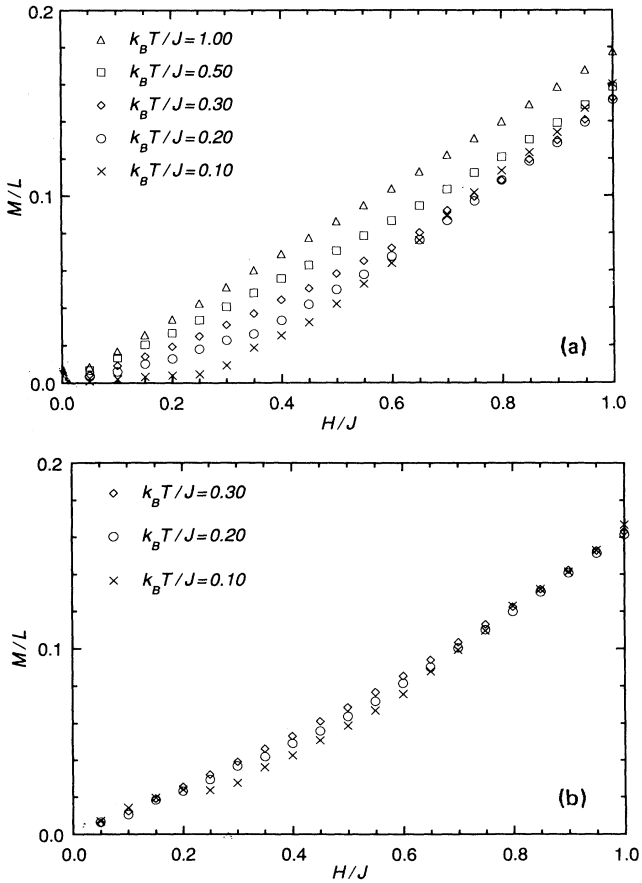

FIG. 2. Low-field magnetization versus magnetic field H at various temperatures for the periodic chain (a) and for the open chain (b).

Taking the finite temperature $k_BT/J = 0.10$ into account, the increase at $H/J \simeq 0.3 \simeq H_c/J - k_BT/J$ is consistent with the nonmagnetic to magnetic transition expected from Eq. (3.8). However, unfortunately, the temperature $k_BT/J = 0.10$, which is the lowest temperature in our calculation, is not low enough to suggest the anomaly at $H = \Delta E$,[25]

$$M/L \sim (H - \Delta E)^{1/2}, \tag{3.9}$$

predicted by the Luttinger liquid theory.

The temperature dependence of the open-chain magnetization is attributed to the magnetic ground states. The magnetization is not monotonic as a function of temperature. In other words, the magnetization curves at various temperatures cross in the low-field range. This phenomenon leads us to the idea[13] that the open-chain magnetization curve is composed of two distinct terms, namely, the bulk part and the edge contribution.

Now let us analyze quantitatively the contribution of the $S = 1/2$ edge states to the open-chain magnetization. We plot in Fig. 3 both the magnetizations (not per spin) of the periodic chain ($\circ$) and the open chain ($\diamond$) with the differences between them ΔM ($\times$). Figure 3(a) and Fig. 3(b) are for $k_BT/J = 0.10$ and for $k_BT/J = 0.20$, respectively. The quantities ΔM can be regarded as the contribution of an extra spin in the open chain. In order to study how this extra moment contributes to the open-chain magnetization, we have also indicated in Fig. 3 two types of Brillouin functions. One is the double of the Brillouin function for $S = 1/2$,

$$\Delta M = \tanh[H/2k_BT], \tag{3.10}$$

which is represented by the solid line, and the other is the Brillouin function for $S = 1$,

$$\Delta M = \frac{2\sinh[H/k_BT]}{1 + 2\cosh[H/k_BT]}, \tag{3.11}$$

which is represented by the broken line. We find that in both Figs. 3(a) and 3(b) the low-field magnetization coming from the extra moment $\Delta M(H)$ is better fitted by the double of the $S = 1/2$ Brillouin function, rather than the single $S = 1$ Brillouin function. This is strong evidence of the appearance of two effective moments of $S = 1/2$ in the chain boundaries.[15,16] However, more careful observation of Fig. 3 shows that $\Delta M(H)$ deviates less from the solid line at $k_BT/J = 0.10$ than at $k_BT/J = 0.20$. This fact can be understood by recognizing that the edge state is well formed at sufficiently low temperatures $k_BT \ll \Delta E$. We note that the $S = 1/2$ moment induced in the boundary is not owing to a single spin but is an effective moment composed of many correlated spins.[15,16] According to Eq. (3.10), ΔM should be saturated toward unity at $H/2k_BT \simeq 2$. Actually, at $k_BT/J = 0.1$, ΔM grows considerably. However, at finite temperatures, ΔM once decreases above the effective critical field $H_c^{\rm eff} \simeq 0.4J - k_BT$ due to the delocalization of the edge moments, which is further discussed in the final section. If we could study the magnetization at lower temperatures, saturation should be realized below the field $H_c^{\rm eff}$.

IV. SUMMARY AND DISCUSSION

We have investigated the temperature dependence of the magnetization process of the $S = 1$ Haldane antiferromagnet. It has been revealed that there is an essential difference for the magnetization process between the periodic chain and the open chain. This difference is attributed to the ground state properties of the periodic and open chains. The ground state of the periodic chain is unique and nonmagnetic, while the open chain has quasifourfold degenerate ground states including magnetic ones.[26] The quantitative analysis of the magnetization difference ΔM has made clearer the picture of the edge moments inherent in the open chains.

Let us consider again the field dependence of ΔM. We show in Fig. 4 the full process of ΔM as a function of H at $k_BT/J = 0.10$. Here we find three distinct field ranges. In the low-field range $H \lesssim H_c^{\rm eff} \simeq 0.3$, the increase of ΔM is well attributed to the two $S = 1/2$ mo-

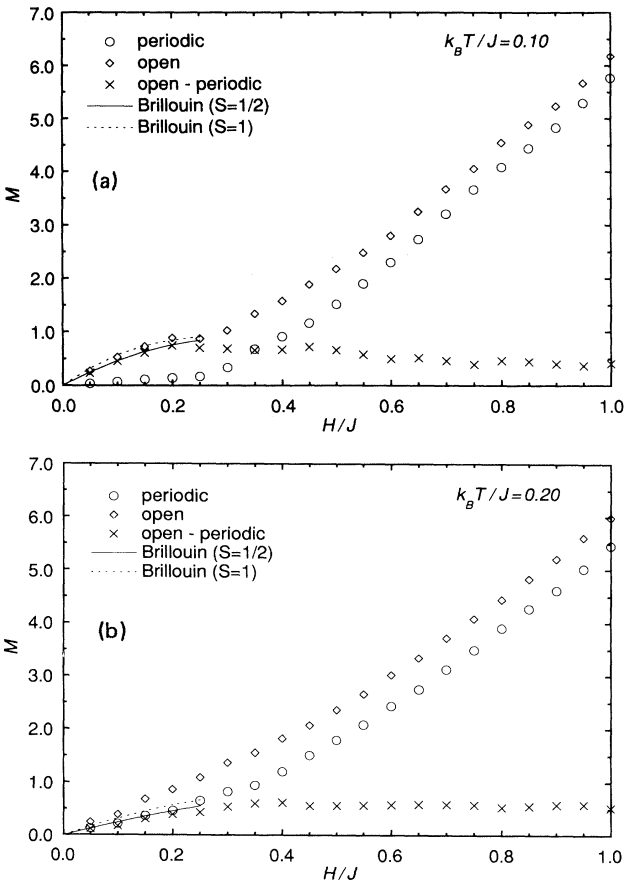

FIG. 3. Comparison of the periodic-chain magnetization and the open-chain magnetization in the low-field range at $k_BT/J = 0.10$ (a) and at $k_BT/J = 0.20$ (b), where the magnetization difference ΔM obtained by subtracting the periodic-chain magnetization from the open-chain magnetization is also represented by $\times$. The solid line describes the double of the Brillouin function for $S = 1/2$ and the broken line describes the Brillouin function for $S = 1$.

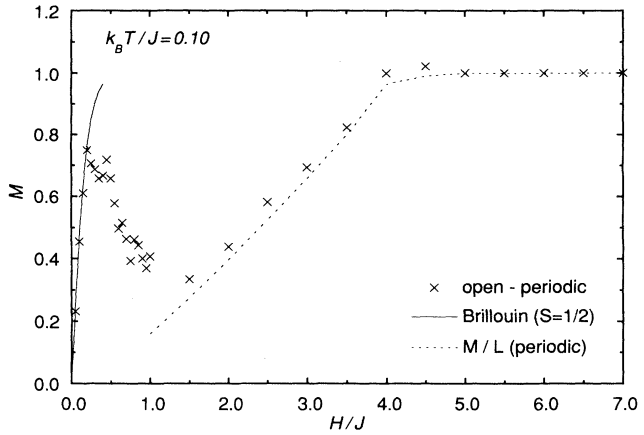

FIG. 4. Full process of the magnetization difference ΔM as a function of magnetic field H ($\times$) at $k_BT/J = 0.10$. The solid and broken lines represent the double of the Brillouin function for $S = 1/2$ and the per-spin magnetization curve for the periodic chain, respectively.

ments at the chain ends, as has been discussed already in the last section. In Fig. 4 we have again indicated the double of the Brillouin function for $S = 1/2$ by the solid line. The behavior of ΔM in this region is therefore inherent in the Haldane phase. In the high-field range $H/J \gtrsim 1.0$, the system is not in the Haldane phase any more and the localized moments at the chain ends do not exist. Therefore the boundary condition is not relevant and ΔM is simply attributed to the difference of the numbers of spins. We have also indicated in Fig. 4 the per-spin magnetization curve for the periodic chain at $k_BT/J = 0.10$ by the broken line, which shows good agreement with ΔM. The field range between the above two, $0.3 \lesssim H/J \lesssim 1.0$, is a transitional range. Due to the collapse of the edge states, ΔM once decreases. It should be noted that the influence of the Haldane phase remains far beyond the critical field. According to the observation of the magnetization, the system is free from the Haldane phase only above a field twice or more as much as the critical field.

In previous papers,[19–21] the present authors have investigated in detail the temperature dependence of the magnetic susceptibility of the present model and demonstrated that with decrease of temperature, the open-chain susceptibility diverges, while the periodic-chain one vanishes. They have further shown that the diverging part which is obtained by subtracting the susceptibility of the periodic chain with L spins from that of the open chain with $L + 1$ spins is well explained as a form $2(1/3)[S(S + 1)J/k_BT]_{S=1/2}$, rather than a form $(1/3)[S(S + 1)J/k_BT]_{S=1}$. From all these results, we could say that the magnetic behavior of the present model with open boundaries is generally explained by a sum of two distinct contributions coming from the bulk and the chain ends.

ACKNOWLEDGMENTS

The authors would like to thank Dr. N. Fujiwara for valuable discussion. The authors are also grateful to Dr. N. Fujiwara and Dr. H. Kikuchi for furnishing copies of their unpublished papers. Numerical calculations were performed on a DEC Alpha station in Osaka University. The present work is supported in part by Grants-in-Aid for Encouragement of Young Scientists (06740289) and for General Scientific Research (06640503), from the Ministry of Education, Science and Culture.

[1] F. D. M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983); Phys. Lett. **93A**, 464 (1983).
[2] R. Botet and R. Julien, Phys. Rev. B **27**, 613 (1983); R. Botet, R. Julien, and M. Kolb, *ibid.* **28**, 3914 (1983); T. Sakai and M. Takahashi, *ibid.* **42**, 1090 (1990); O. Golinelli, Th. Colicoeur, and R. Lacaze, Phys. Rev. B **50**, 3037 (1994).
[3] R. M. Nightingale and H. W. J. Blöte, Phys. Rev. B **33**, 6545 (1986); M. Takahashi, *ibid.* **38**, 5188 (1988); Phys. Rev. Lett. **62**, 2313 (1989); K. Nomura, Phys. Rev. B **40** 2421 (1989).
[4] K. Kubo and S. Takada, J. Phys. Soc. Jpn. **55**, 438 (1986); H. Betsuyaku, Phys. Rev. B **34**, 8125 (1986); K. Kubo, *ibid.* **46**, 866 (1992).
[5] S. R. White and D. A. Huse, Phys. Rev. B **48**, 3844 (1993).
[6] J. P. Renard, M. Verdaguer, L. P. Regnault, W. A. C. Erkens, J. Rossat-Mignod, and W. G. Stirling, Europhys. Lett. **3**, 945 (1987).
[7] K. Katsumata, H. Hori, T. Takeuchi, M. Date, M. Yamagishi, and J. P. Renard, Phys. Rev. Lett. **63**, 86 (1989); Y. Ajiro, T. Goto, H. Kikuchi, T. Sakakibara, and T. Inami, *ibid.* **63**, 1424 (1989).
[8] J. B. Parkinson and J. C. Bonner, Phys. Rev. B **32**, 4703 (1985).
[9] R. P. Hodgson and J. B. Parkinson, J. Phys. C **18**, 6385 (1985).
[10] T. Sakai and M. Takahashi, Phys. Rev. B **43**, 13 383 (1991).
[11] T. Delica, K. Kopinga, H. Leschke, and K. K. Mon, Europhys. Lett. **15**, 55 (1991).
[12] J. P. Renard, V. Gadet, L. P. Regnault, and M. Verdaguer, J. Magn. Magn. Mater. **90&91**, 213 (1990).
[13] H. Kikuchi, Y. Ajiro, N. Mori, H. Aruga-Katori, T. Goto, and H. Nagasawa, Physica B **201**, 186 (1994); N. Fujiwara, J. R. Jeitler, C. Navas, M. M. Turnbull, T. Goto, and N. Hosoito, J. Magn. Magn. Mater. (to be published).
[14] I. Affleck, T. Kennedy, E. H. Lieb, and H. Tasaki, Phys. Rev. Lett. **59**, 799 (1987); Commun. Math. Phys. **115**, 477 (1988).
[15] S. R. White and D. A. Huse, Phys. Rev. B **48**, 3844 (1993); S. R. White, *ibid.* **48**, 10 345 (1993).
[16] S. Miyashita and S. Yamamoto, Phys. Rev. B **48**, 913 (1993).
[17] M. Suzuki, in *Quantum Monte Carlo Methods*, edited by M. Suzuki (Springer-Verlag, Heidelberg, 1986), p. 2.
[18] J. E. Hirsch, R. L. Sugar, D. J. Scalapino, and R. Blankenbecler, Phys. Rev. B **26**, 5033 (1982).
[19] S. Yamamoto and S. Miyashita, Phys. Rev. B **50**, 1 6277 (1994).
[20] S. Yamamoto and S. Miyashita, Phys. Rev. B **48**, 9528 (1993).

[21] S. Miyashita and S. Yamamoto, J. Phys. Soc. Jpn. **62**, 1459 (1993).
[22] T. Takeuchi, H. Hori, T. Yoshida, A. Yamagishi, K. Katsumata, J. P. Renard, V. Gadet, M. Verdaguer, and M. Date, J. Phys. Soc. Jpn. **61**, 3262 (1992).
[23] S. Katsura and M. Suzuki, J. Phys. Soc. Jpn. **28**, 255 (1970).
[24] I. Affleck, Phys. Rev. B **41**, 6697 (1990).
[25] T. Sakai and M. Takahashi, J. Phys. Soc. Jpn. **60**, 3615 (1991).
[26] T. Kennedy, J. Phys. Condens. Matter **2**, 5737 (1990).