String correlations of the antiferromagnetic spin-1 chain: Excited states and magnetic-field effects

N. Elstner
Physics Department, University of California, Santa Cruz, California 95064

H.-J. Mikeska
Institut für Theoretische Physik, Universität Hannover, 30167 Hannover, Germany
(Received 24 September 1993; revised manuscript received 22 February 1994)

We calculate energies and wave functions of $S = 1$ antiferromagnetic Heisenberg chains with single-ion anisotropy in a symmetry-breaking external magnetic field. From results for the string correlation function for low-lying excited states we identify these states as solitons with respect to the hidden string order. For finite anisotropic chains we investigate the transition to the fully magnetized state at high magnetic fields and conclude that Bose condensation in an external magnetic field occurs also for the anisotropic chain.

I. INTRODUCTION

It is now widely accepted that the ground state of the isotropic antiferromagnetic $S = 1$ chain is disordered and separated by a finite gap from the lower edge of the excitation continuum at wave number $k = \pi$. Originally this was conjectured by Haldane,[1] who argued that this behavior is a general feature of one-dimensional antiferromagnets with integer spin S. This behavior is in sharp contrast to that of chains with half-integer spin where a gapless spectrum and an algebraic decay of correlations are expected as is known from the exactly solvable $S = \frac{1}{2}$ problem. Although there is still no mathematical proof of Haldane's conjecture, numerical studies (exact diagonalization of small systems and quantum Monte Carlo simulations[2–5]) have left little doubt that a "Haldane phase" with the described properties really exists in some region of parameter space including a neighborhood of the isotropic Heisenberg antiferromagnet.

In the past few years much progress has been made in understanding the nature of the ground state in the Haldane phase. There exists one model, with additional biquadratic exchange, whose ground state is exactly solvable, giving an example of a Haldane state.[6] Furthermore, Kennedy and Tasaki[7] have shown that the $S = 1$ Hamiltonian contains a hidden $Z_2 \otimes Z_2$ symmetry. The complete breaking of this hidden symmetry characterizes the Haldane phase and is described by a nonlocal order parameter introduced earlier by den Nijs and Rommelse[8] in the context of surface roughening. Numerical calculations of this "string order parameter" have indeed established finite values for this quantity in the Haldane ground state.[9,10]

Investigations for excited states have mostly concentrated on calculations of the spectrum. Besides efforts to determine the gap at $k = \pi$, special attention has been focused on the lowest excited state with $k = 0$, because the O(3) nonlinear σ model predicts that this state should consist of two elementary excitations with $k = \pi$. Thus the gap at $k = 0$ should be twice the gap at $k = \pi$.[11] This also follows from the approximate mapping of the Haldane chain to a fermion or effective $S = \frac{1}{2}$ chain[12,13] and has been confirmed by Monte Carlo simulations and exact diagonalization studies.[4,5]

In this paper we investigate the Heisenberg antiferromagnetic chain with single-ion anisotropy in an external symmetry-breaking magnetic field as described by the Hamiltonian:

$$H = \sum_n \mathbf{S}_n \cdot \mathbf{S}_{n+1} + D \sum_n (S_n^z)^2 - B_x \sum_n S_n^x$$
$$= H_{\mathrm{exc}} + H_D + H_Z \,. \tag{1}$$

The $\mathbf{S}_n$ are spin-1 operators placed on a chain with periodic boundary conditions. We have calculated the energies and the spin and string correlation functions of the ground state and some of the lowest excited states with $k = 0$ and $k = \pi$. Our results for energies and wave functions were obtained on an IBM RS6000 workstation using a Lanczos algorithm to diagonalize finite chains with up to 16 sites (up to 18 sites for the case with conserved S_{tot}^x). The maximum number of sites, $N_{\mathrm{max}} = 18$ and 16, respectively, is the current limitation from the available memory space and agrees with the maximum chain length treated in previous calculations.[5,14] Much longer chains can be dealt with in good approximation by the recently developed density matrix approach;[15,16] this approach, however, is not well suited for nonlocal operators, such as string correlators. Therefore, for a discussion of the string correlations, we found it appropriate to use the standard diagonalization approach, which gives the exact results for chains up to 18 sites.

There exist several magnetic chain materials, which are good candidates for a realization of a Haldane phase in nature. Among these, $CsNiCl_3$ (Refs. 17, 18) and

0163-1829/94/50(6)/3907(6)/$06.00

$Ni(C_2H_8N_2)_2NO_2CLO_4$ (NENP) (Ref. 19) are the most prominent ones. Experiments in an external magnetic field B have been done in some detail for NENP and extrapolate to a gap vanishing at some critical field B_c.[20] For a full account of the behavior of this material, single-ion anisotropies have to be taken into account, whereas $CsNiCl_3$ is to a high degree isotropic.

Energies of the low-lying states of small chains for magnetic fields $B < B_c$ were recently calculated by Golinelli *et al.*[14] using the Hamiltonian appropriate for NENP. They found good agreement with experimental results[20] for NENP and we reproduce their results. In addition we have calculated the correlation functions and also considered values of the magnetic field $B > B_c$.

From our numerical data we present the following results.

(i) String correlations for the lowest excited states will be discussed for the isotropic chain ($D = 0, B_x = 0$) in Sec. II. From our results we find numerical evidence that the lowest excited state of the Haldane chain is appropriately described as a soliton in the string order.

(ii) The effect of a symmetry-breaking magnetic field in the anisotropic chain ($D \neq 0, B_x \neq 0$) will be discussed in Sec. III. The phase transition at a critical magnetic field $B_x = B_c$, which has been discussed for the isotropic model,[21,22] is found to correspond to a smooth crossover in the string correlations. The Bose condensation at the critical field is shown to persist when anisotropy is included.

Translation and reflection symmetry allow us to classify the eigenstates of the system by wave number k and parity $R = \pm$. For the isotropic model ($D = 0$, $B_x = 0$) the total spin of the chain $\mathbf{S}^2_{\rm tot}$ and one of its components, e.g., $S^x_{\rm tot}$, are conserved. In the case $D \neq 0$, $B_x = 0$ ($D = 0$, $B_x \neq 0$) only the component of total spin $S^z_{\rm tot}$ ($S^x_{\rm tot}$) remains a good quantum number. In the general case, $D \neq 0$ and $B_x \neq 0$, and there is no conserved component of spin, but the spin flip parity

$$P_{\rm SF} = \exp[i\pi S^x_{\rm tot}] \tag{2}$$

survives as good quantum number. $P_{\rm SF}$ commutes with the Hamiltonian since $H_{\rm exc}$ and H_Z do not change $S^x_{\rm tot}$ at all, whereas H_D does change $S^x_{\rm tot}$ by either zero or ± 2. The possibility to classify eigenstates by the spin flip parity $P_{\rm SF}$ reflects the invariance of the system under reflections in spin space perpendicular to the external field.

From the wave functions of the lowest states we have calculated the following quantities: (i) the magnetization

$$m^x = \left\langle \sum_n S^x_n \right\rangle , \tag{3}$$

(ii) the spin correlation functions

$$S^{\alpha,\alpha}(n) = \frac{1}{N} \left\langle \sum_i S^\alpha_i S^\alpha_{i+n} \right\rangle , \quad \alpha = x, y, z, \tag{4}$$

(iii) and the string correlation functions

$$T^{\alpha,\alpha}(n) = \frac{1}{N} \left\langle \sum_i S^\alpha_i \exp\left[i\pi \sum_{j=i+1}^{i+n} S^\alpha_j \right] S^\alpha_{i+n} \right\rangle ,$$

$$\alpha = x, y, z. \tag{5}$$

There exist some trivial identities between the string and spin correlation functions for $n = 0, 1$ and between spin as well as string correlation functions at sites related by reflection symmetry, n and $N - n$. We have used these identities to make sure that our numerical results are consistent. The numerical accuracy of our results can also be checked by comparing the quantity

$$N \sum_\alpha \{S^{\alpha,\alpha}(1) + DS^{\alpha,\alpha}(0)\} - B_x m^x,$$

with the energy E as calculated by the Lanczos routine. For the lowest state in each subspace the two numbers differ by slightly less than 10^{-6} (for chains with 8 and 16 sites the two results actually agree up to 10^{-12}).

II. STRING CORRELATIONS AT THE ISOTROPIC POINT

For the isotropic model (D=0) the conservation of $S^x_{\rm tot}$ enables us to deal with chains with up to 18 sites. Also, it is sufficient to do calculations for the case of zero field only, because every simultaneous eigenstate of $H_{\rm exc}$ and $S^x_{\rm tot}$ will remain an eigenstate at finite B_x.

The ground state in the Haldane phase is a singlet with wave number $k = 0$ and parity $R = +$. In zero field the first excited states form a triplet (Haldane triplet) with $k = \pi$ and $R = -$. In the $k = 0$ sector the first excited states have $S_{\rm tot} = 2$ and transform even under spatial reflections, $R = +$. Furthermore we have calculated the multiplets with ($S_{\rm tot} = 3$, $k = \pi$, $R = -$) and ($S_{\rm tot} = 4$, $k = 0$, $R = +$), because these can be considered approximately as three- (respectively four-) particle excitations.[21,22] From the fact that the correlation length is known to be of the order of six lattice sites it is clear that qualitative information only can be obtained from our limited chain length calculations for states with more than one excitation.

We have calculated correlation functions for the two lowest states with $k = 0$ ($S = 0$ and $S = 2$) and the lowest state with $k = \pi$ ($S = 1$). The presence of the magnetic field has the effect of selecting from the corresponding multiplet as the lowest state that with the maximum value of $S^x_{\rm tot}$. Therefore the data for the excited states are for $S^x_{\rm tot}$ equal to 1 and 2, respectively. Only for the excited states with $S^x_{\rm tot} \neq 0$ do we have to distinguish between longitudinal and transverse correlations. Figure 1 shows our results for the longitudinal (parallel to the external field) string correlations $T^{x,x}(n)$. The results as shown are the original data of the chain with 18 sites for the three states.

For the Haldane ground state ($S^x_{\rm tot} = 0$ for magnetic fields below the Haldane gap) we reproduce results as found by other groups: The spin correlations decay quite

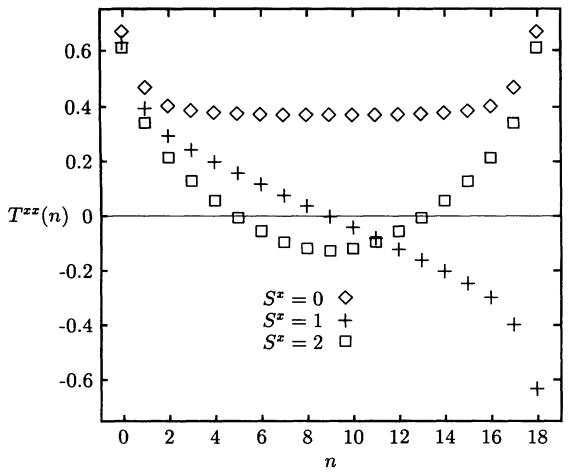

FIG. 1. String correlation function $T^{x,x}(n)$ parallel to the quantization axis for the ground state ($S^x = 0$) and the two lowest excited states ($S^x = 1, 2$) of the isotropic (D=0) chain with 18 sites.

rapidly (the correlation length has been estimated to be about six lattice spacings) while the string correlations go to a finite asymptotic value:

$$\lim_{n\to\infty} T^{x,x}(n) \approx 0.37.$$

It should be noted that this numerical value is quite well reproduced by the approximate theory of Kennedy and Tasaki,[7] which gives $\frac{4}{9}$ as asymptotic value (for the isotropic Hamiltonian, independent of the strength of biquadratic exchange).

We now proceed to a discussion of the behavior of $T^{x,x}$ in the lowest excited state: From Fig. 1 we see that $T^{x,x}(n)$ for $S^x_{\rm tot} = 1$ changes sign for $n = N/2$. This result allows us to characterize the lowest excited state as a one-soliton state: The ground state has broken symmetry with respect to the (nonlocal) string order parameter and the simplest excited state is characterized by a localized region where a transition between two possible values of this order parameter takes place. The wave function of this state can be calculated in the mean-field approximation of Kennedy and Tasaki[7] and leads to the following expression for the string correlation function ($n \neq 0, N$):[23]

$$T^{x,x}(n) = \text{const} \times (1 - 2n/N) \,. \tag{6}$$

The numerical data as shown in Fig. 1 are in very good agreement with this analytical result following from the soliton character of the excited state. Excited states of this type have previously been suggested[24] for the antiferromagnetic chain with additional biquadratic interaction, which has an exactly solvable ground state.[6]

For higher excited states our calculations have only qualitative significance since due to the limited chain length the interaction between elementary excitations will be overemphasized; nevertheless, our results fit into the picture just described.

The string correlations show periodic changes in sign, which are correlated with the total magnetization $S^x_{\rm tot}$. For $S^x_{\rm tot} = m$, $m = 3, 4$, the string correlations change their sign m times when going once around the chain. This behavior of $T^{x,x}(n)$ can be interpreted as an indication of the multiparticle character of the excited states, with each elementary excitation changing the sign of the order parameter once. Thus, our data can be considered as qualitative evidence supporting the field theoretic predictions about the excitation spectrum. In contrast to the results of Ref. 16 these results do not test the problem of m elementary excitations in the dilute regime; here interactions have strong effects for $m > 1$. On the other hand, the string correlation function shows much more directly than the local magnetization[16] the qualitative effect of elementary excitations on the wave functions, even for rather short chains.

The results for the string correlation functions are independent of the magnetic field since the wave functions do not depend on the magnetic field in the isotropic case. The energies, of course, do depend on the external field and at a field strength equal to the Haldane gap the $S^x_{\rm tot} = 1$ component of the $k = \pi$ triplet crosses the Haldane ground state. If excited states at $k = 0, \pi$ are simply composed of the Haldane triplet as the basic elementary excitation, then, in the thermodynamic limit, states with any number of these particles will condense at the same field. What prevents the condensation of states with an arbitrary large number of elementary excitations is the interparticle repulsion.[21,22] For finite chains this interparticle repulsion is observed already for two excitations: Considering the lowest multiplets $S = 0, 1, 2$, the ground state switches from $S = 0, k = 0$ to $S = 1, k = \pi$ at $B = \Delta_1$ and from $S = 1, k = \pi$ to $S = 2, k = 0$ at $B = \frac{1}{2}\Delta_2$, where $\Delta_1 = \Delta_{k=\pi}$ is the Haldane gap and $\Delta_2 = \Delta_{k=0} = 2\Delta_1 + \delta$ is the excitation energy of the two-particle state with $\delta > 0$ due the repulsion in the finite chain. A finite size analysis of the quantities $\frac{1}{m}\Delta_m$ leads to a limit independent of m for this quantity, which is the numerical evidence for Bose condensation in the isotropic chain. This result so far has been obtained only for the isotropic chain—in the following section we will discuss corresponding results for the ansiotropic system.

III. ANISOTROPIC SYSTEM IN A SYMMETRY-BREAKING EXTERNAL FIELD

We now turn to the case of the anisotropic chain, $D \neq 0$, where no component of the total chain spin is conserved for $B_x \neq 0$. As discussed above, the only remaining good quantum numbers are k, R and the spin parity $P_{\rm SF}$; this means that states with even (respectively odd) values of $S^x_{\rm tot}$ now mix. Owing to the reduced symmetry we were only able to perform calculations for chains with up to 16 sites.

In the following we present results for the value $D = 0.2$, which is close to the best known value for NENP, $D = 0.18$. In addition, NENP is characterized by a small in-plane anisotropy, $H_E = -E\sum_i (S^x_i)^2$ with $E \approx 0.02$, which we did not take into account. As before, we have

calculated the ground state ($k = 0, R = +, P_{SF} = +$) and the lowest excited states with $k = \pi$ ($R = -$, $P_{SF} = -$) and $k = 0$ ($R = +$, $P_{SF} = +$). Our data for the energies of these three states in the chain with 14 sites as function of the field are very close to those of Golinelli *et al.*,[14] who calculated the energies of the lowest states with the exact NENP parameters. Due to the reduced symmetry the discontinuous change in the ground state of the isotropic chain is now replaced by a smooth behavior: The energy difference

$$\Delta E(B_x) = E(k = \pi, R = -, P_{SF} = -; B_x) - E(k = 0, R = +, P_{SF} = +; B_x)$$

of the two lowest states now oscillates around zero as shown in Fig. 2. This illustrates that with increasing external field avoided crossings occur; for finite chains the ground state alternates between the two surviving subspaces.

To discuss the phase transition at a critical field B_c and a possible Bose condensation in the anisotropic chain we have followed different approaches.

A critical field $B_c^{(1)}$ is determined from the first zero of $\Delta E(B_x)$ with increasing B_x, $B_c^{(1)} = B_{c,1}$. Values for $B_c^{(1)}$ are given in Table I and extrapolate to $B_c^{(1)} = 0.49 \pm 0.01$ for $N \to \infty$. This result was obtained using a one-parameter family of transformations, introduced by van den Broek and Schwartz (VBS) (for a description see Ref. 25). The free parameter in these transformations was used to determine the error bars. It appears that, although the zero field gap is smaller compared to the isotropic case, the critical field strength is larger.

A critical field $B_c^{(2)}$ is determined from the first avoided crossing in the subspace ($k = 0$, $R = +$, $P_{SF} = +$). The string correlations reflect this avoided crossing as seen from Fig. 3: They show a crossover between the values corresponding to the two lowest states in this subspace. $B_c^{(2)}$ may be defined as the magnetic field at which the string correlations of the two states are equal. For both states the string correlation increases (respectively decreases) linearly near the transition and $B_c^{(2)}$; they are therefore suited better than energy data to determine the critical field. When we approach the isotropic case the crossover in the string correlations becomes increasingly steeper and all characteristic fields trivially agree. In terms of $\Delta E(B_x)$, $B_c^{(2)}$ is to be identified with the magnetic field corresponding to the first minimum of $\Delta E(B_x)$. Numerical values for $B_c^{(2)}$ have again been determined from VBS transformations. However, since the extrapolations are less accurate than for $B_c^{(1)}$ we only mention that the result does not contradict the expectation that all characteristic field strengths are identical also for anisotropic interactions.

TABLE I. Critical field strength $B_c(1)(N)$.

N	$B_c(k = \pi)$
6	0.79038
8	0.67019
10	0.60617
12	0.56867
14	0.54543
16	0.53030
∞	0.49 ± 0.01

The width of the first intermediate phase $\Delta B_c = B_{c,2} - B_{c,1}$, where $B_{c,2}$ is the second zero of $\Delta E(B_x)$, characterizes the influence of particle interactions and finite size effects on the Bose condensation. In the isotropic case this width extrapolates to zero in the thermodynamic limit. In order to see whether this is the case for the anisotropic chain as well, we have investigated ΔB_c in a finite size analysis as shown in Fig. 4, where the width $\Delta B_c(N)$ of the first phase with $k = \pi$ is plotted versus $1/N$. For comparison the data of the isotropic system [$\Delta B_c(N) = \Delta_{k=0}(N) - 2\Delta_{k=\pi}(N)$] are included. The actual data are listed in Table II. We see that this width extrapolates to zero for $N \to \infty$ and we conclude that the description of the phase transition in terms of a Bose condensation as given by Sørensen and Affleck[22,16] is consistent with the numerical data also for a symmetry-breaking magnetic field. Assuming only a $1/N$ depen-

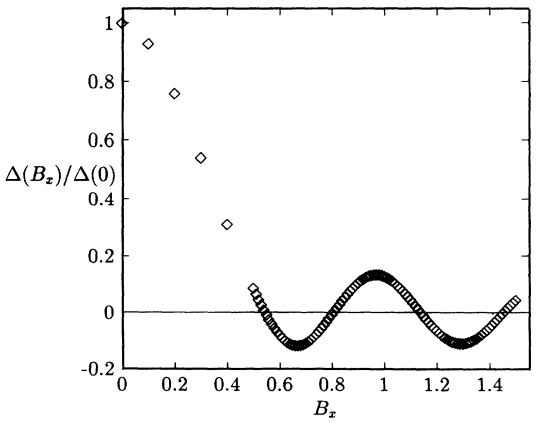

FIG. 2. Normalized excitation gap $\Delta E(B_x)/\Delta E(0)$ [$\Delta E(B_x) = E(k = \pi, B_x) - E(k = 0, B_x)$] for the anisotropic chain (D=0.2) with 14 sites as function of the external field.

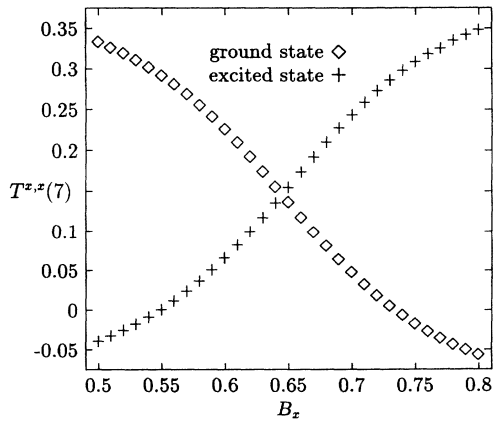

FIG. 3. String correlation function $T^{x,x}(7)$ parallel to the field for the ground state and the lowest excited state with $k = 0$ of the anisotropic chain (D=0.2) with 14 sites as function of the external field B_x.

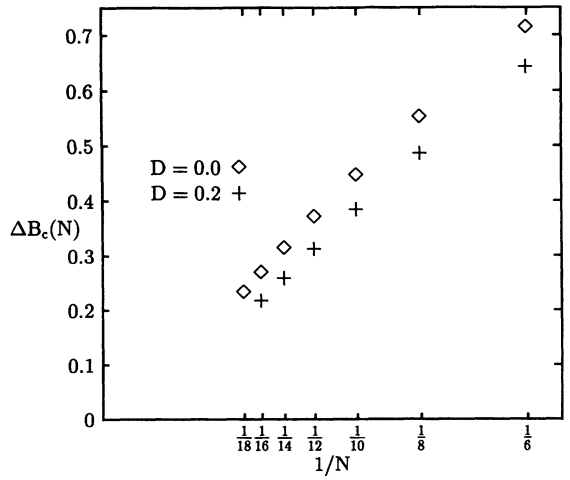

FIG. 4. The width ΔB_c of the first intermediate phase with a $k = \pi$ ground state vs $1/N$. The data shown are for the isotropic (D=0.0) and the anisotropic chain (D=0.2).

dence of finite size effects gives slightly negative values for $N \to \infty$. Obviously higher-order corrections are still important. An estimate of the thermodynamic limit using the same type of VBS transforms agrees with the expectation that ΔB_c will vanish.

IV. CONCLUSIONS

We have successfully applied the concept of a hidden (string) order parameter to the excited states of the antiferromagnetic spin-1 chain. We have found that the elementary excitations in the Haldane phase have a characteristic effect on the string order: Each such particle produces one change of sign for the variation of the order parameter correlation function with distance. On this basis we interpret the elementary excitations as solitons with respect to the string order. The discussion in terms of the string order parameter is thus the most adequate presentation of the wave function of the low-lying excited states.

We have also considered the effect of an external magnetic field on energies and wave functions of the Haldane ground state and the low-lying excited states. An external field decreases the energy of excited multiparticle states until at a critical field $B_c \approx \Delta_{k=\pi}$ the Zeeman energy compensates the particle "rest mass" and a phase transition occurs. In the isotropic limit (and equally in the case of rotationally invariant anisotropies), interactions between the elementary excitations are essential to lift the degeneracy at B_c of the Haldane ground state and the multiparticle states and to establish the new state as described by Tsvelick[21] and Affleck.[22] For finite values of N these processes occur as a sequence of discrete steps.

TABLE II. Width $\Delta B_c(N)$ of the first intermediate phase with $k = \pi$ for finite chains.

N	$D = 0.0$	$D = 0.2$
6	0.71445	0.64414
8	0.55329	0.48797
10	0.44746	0.38599
12	0.37173	0.31386
14	0.31448	0.26012
16	0.26958	0.21883
18	0.23344	
∞	0.01 ± 0.03	0.02 ± 0.04

For the anisotropic chain without rotational symmetry with respect to the magnetic field, degeneracies are lifted not only by interactions but also by the coupling between all states with a given spin flip parity: The multiparticle states no longer differ by quantum numbers related to rotational symmetry; there are only two subspaces left, corresponding to even and odd values of $S^z_{\rm tot}$. In the thermodynamic limit we again have found degeneracy, indicating a Bose condensation as in the isotropic case. This result then establishes the interpretation of the excitation spectrum in terms of elementary excitations also for the anisotropic case.

ACKNOWLEDGMENT

One of us (N.E.) acknowledges support by the Deutsche Forschungsgemeinschaft.

[1] F.D.M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983); Phys. Lett. **93A**, 464 (1983).
[2] R. Botet, R. Jullien, and M. Kolb, Phys. Rev. B **28**, 3914 (1983).
[3] T. Sakai and M. Takahashi, Phys. Rev. B **42**, 1090 (1990); **42**, 4537 (1990).
[4] M. Takahashi, Phys. Rev. Lett. **62**, 2313 (1989).
[5] O. Golinelli, Th. Jolicœur, and R. Lacaze, Phys. Rev. B **46**, 10 854 (1992).
[6] I. Affleck, T. Kennedy, E.H. Lieb, and H. Tasaki, Phys. Rev. Lett. **59**, 799 (1987); Commun. Math. Phys. **115**, 583 (1988).
[7] T. Kennedy and H. Tasaki, Phys. Rev. B **45**, 304 (1992).
[8] M. den Nijs and K. Rommelse, Phys. Rev. B **40**, 4709 (1989).
[9] S.M. Girvin and D.P. Arovas, Phys. Scr. T **27**, 156 (1989).
[10] Y. Hatsugai and M. Kohmoto, Phys. Rev. B **44**, 11 789 (1991).
[11] I. Affleck, J. Phys. Condens. Matter **1**, 3047 (1989).
[12] G. Gómez-Santos, Phys. Rev. Lett. **63**, 790 (1989).
[13] H.-J. Mikeska, Europhys. Lett. **19**, 39 (1992).
[14] O. Golinelli, Th. Jolicœur, and R. Lacaze, J. Phys. Condens. Matter **5**, 7847 (1993).
[15] S.R. White, Phys. Rev. Lett. **69**, 2863 (1992).
[16] E.S. Sørensen and I. Affleck, Phys. Rev. Lett. **71**, 1633 (1993).
[17] K. Kakurai, M. Steiner, R. Pynn, and J.K. Kjems, J. Phys. Condens. Matter **3**, 715 (1991).

[18] Z. Tun, W J.L. Buyers, A. Harrison, and J.A. Rayne, Phys. Rev. B **43** 13 331 (1991).
[19] J.P. Renard, M. Verdaguer, L.P. Regnault, W.A.C. Erkelenz, J. Rossat-Mignod, J. Ribas, W.G. Stirling, and C. Vettier, J. Appl. Phys. **63**, 3538 (1988).
[20] L.P. Regnault, C. Vettier, J. Rossat-Mignod, and J.P. Renard, Physica B **180-181**, 188 (1992).
[21] A.M. Tsvelik, Phys. Rev. B **42**, 10 499 (1990).
[22] I. Affleck, Phys. Rev. B **43**, 3215 (1991).
[23] H.-J. Mikeska and U. Neugebauer (unpublished).
[24] S. Knabe, J. Stat. Phys. **52**, 627 (1988).
[25] N.M. Barber, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J.L. Lebowitz (Academic, London, 1983), Vol. 8.