Low-Energy Structure of Heisenberg Ferrimagnetic Spin Chains

Shoji YAMAMOTO and Tôru SAKAI

Department of Physics, Faculty of Science, Okayama University,
Okayama, Okayama 700-8530

Faculty of Science, Himeji Institute of Technology,
Kamigori, Ako, Hyogo 678-1297

(Received 21 August 1998)

Static and dynamic structure factors of Heisenberg ferrimagnetic spin chains are numerically investigated. There exist two distinct branches of elementary excitations, which exhibit ferromagnetic and antiferromagnetic aspects. The ferromagnetic feature is smeared out with the increase of temperature, whereas the antiferromagnetic one persists up to higher temperatures. The scattering intensity is remarkably large at lower boundaries of the ferromagnetic and antiferromagnetic spectra. All these observations are consistent with the ferromagnetic-to-antiferromagnetic crossover in the thermal behavior which has recently been reported.

KEYWORDS: ferrimagnetic spin chain, static structure factor, dynamic structure factor, quantum Monte Carlo, exact diagonalization

Recently considerable attention has been directed to quantum magnets with two kinds of antiferromagnetically exchange-coupled centers. Since coexistent spins of different kinds do not necessarily result in magnetic ground states, it remains a stimulating problem whether the system is massive or massless. For example, an alignment of elementary cells with spins 1, 1, 1, and 1/2 in this order results in a singlet ground state and an excitation gap immediately above it. Several authors have generally discussed what is the criterion for the massive phases via the nonlinear- \( \sigma \)-model technique. Several authors have already discussed the-

\[ \mathcal{H} = J \sum_j (S_j \cdot s_j + s_j \cdot S_{j+1}) , \]

show ferrimagnetism instead of antiferromagnetism. Considering that all the mixed-spin-chain compounds synthesized so far exhibit ferrimagnetic ground states, the study on the model (1), the simplest example of a quantum ferrimagnet, is all the more important. Although pioneering authors have already discussed theoretically quantum ferrimagnets in the 1980s, their interest was, for instance, the quantitative dependence of the thermal behavior on constituent spin quantum numbers. The exact diagonalization of short chains was not necessarily conclusive in understanding the universal quantum ferrimagnetic behavior especially at low temperatures. Recent arguments have renewed the interest in this fascinating subject and have even motivated brand-new NMR measurements which are currently in progress.

Let us consider the Hamiltonian (1) under the periodic boundary condition. We set the number of unit cells to \( N \) and assume that \( S > s \). Then the Lieb-Mattis theorem immediately shows that the Hamiltonian (1) has ferrimagnetic ground states of spin \((S-s)N\). As we may generally expect gapless excitations from magnetic ground states, we here take little interest in the naive problem of whether the spectrum is gapped or gapless. Actually, gapless excitation branches lie in the subspace whose total spin is less than \((S-s)N\), showing quadratic dispersion relations at small momenta. Thus the low-lying excitations of quantum ferrimagnets have a ferromagnetic aspect. The other excitation branches lying in the subspace whose total spin is greater than \((S-s)N\) are all gapped and reminiscent of gapped antiferromagnets.

The thus-revealed low-energy structure may be recognized as a combination of ferromagnetic and antiferromagnetic features and is well explained in terms of the spin-wave theory. For the sake of argument, we briefly review the spin-wave treatment. We introduce the bosonic operators for the spin deviation from a Néel state with \( M = \sum_j (S_j^x + s_j^x) = (S-s)N \) as

\[ S_j^+ = \sqrt{2S} a_j , \quad S_j^z = S - a_j^\dagger a_j , \]
\[ s_j^+ = \sqrt{2s} b_j^\dagger , \quad s_j^z = -s + b_j b_j^\dagger . \]

Setting the lattice constant to \( a \), we define the momentum representation of the bosonic operators as

\[ a_k = \frac{1}{\sqrt{N}} \sum_j e^{2\pi i k (j-1/4)} a_j , \]
\[ b_k = \frac{1}{\sqrt{N}} \sum_j e^{-2\pi i k (j+1/4)} b_j . \]

The Bogoliubov transformation

\[ \alpha_k = \cos \theta_k a_k + \sin \theta_k b_k^\dagger , \]
\[ \beta_k = \sin \theta_k a_k^\dagger + \cos \theta_k b_k , \]

with

\[ \tanh 2 \theta_k = -\frac{2 \sqrt{S s}}{S + s} \cos(ak) , \]
results in the two distinct dispersion relations
\[ \omega_k^\pm = \omega_k \mp (S-s) , \]
where
\[ \omega_k = \sqrt{(S-s)^2 + 4Ss \sin^2(ak)} . \]
The \( \alpha \)- and \( \beta \)-bosons, respectively, have the effects of reducing and enhancing the ground-state magnetization and may therefore be regarded as ferromagnetic and antiferromagnetic. The obtained dispersions \( \omega_k^+ \) and \( \omega_k^- \) are indeed reminiscent of those of ferromagnets and gapped antiferromagnets, respectively, though the antiferromagnetic gap within the lowest-order spin-wave theory, \( \omega_k = |J| \), is much smaller than the true value \( \Delta = 1.75 J \).

Two distinct features are most prominently exhibited in the temperature dependence of the specific heat. At low temperatures a ferromagnetic \( T^{1/2} \) initial behavior appears, whereas at intermediate temperatures we encounter a Schottky-like peak which can simply be described by the antiferromagnetic gap \( \Delta \). Motivated by these observations, we here investigate the low-energy structure of quantum ferrimagnets in detail. Although the low-lying antiferromagnetic excitations lie in the background of the ferromagnetic spectra, why does such a well-pronounced Schottky-like peak appear? This is the subject in the present article. Since previous numerical investigations\cite{1,2} suggest that quantum behavior of the model (i) is qualitatively the same regardless of the values of \( S \) and \( s \) as long as they differ from each other, we restrict our argument to the case of \( (S, s) = (1, 1/2) \).

In order to reveal how the ferromagnetic and antiferromagnetic aspects are exhibited, we here investigate static structure factors as functions of temperature. Generally, the static structure factors of ferromagnetic mono-spin chains have their peaks at the zone center \( k = 0 \), while those of antiferromagnetic mono-spin chains at the zone boundary \( k = \pi/a \). However, in the present case, the system is composed of two interacting sublattices and both ferromagnetic and antiferromagnetic peaks appear at the center of the reduced Brillouin zone \( -\pi/2a < k \leq \pi/2a \). Therefore the position of the peak can not be used to determine its nature. In an attempt to find relevant operators to detect the ferromagnetic and antiferromagnetic modes, we here rely on the spin-wave theory, namely, we regard the \( \alpha \)-boson and \( \beta \)-boson correlations as ferromagnetic and antiferromagnetic, respectively. Keeping in mind that the present model is isotropic, thermal averages \( \langle \alpha_k \rangle \) and \( \langle \beta_k \rangle \) can be calculated in terms of spin operators as
\[
\langle \alpha_k \rangle = S^-(k) = \langle O^- \rangle , \quad \langle \beta_k \rangle = S^+(k) = \langle O^+ \rangle ,
\]
with
\[
O^- = \cosh \theta_k S^- + \sqrt{2} \sinh \theta_k S^z , \quad O^+ = \sinh \theta_k S^- + \sqrt{2} \cosh \theta_k S^z ,
\]
where the Fourier transforms of the spin operators are generally defined as
\[
S^\lambda_k = \frac{1}{\sqrt{N}} \sum_j e^{2iak(j-1/4)} S^\lambda_j , \quad S^\lambda_j = \frac{1}{\sqrt{N}} \sum_k e^{2iak(j+1/4)} S^\lambda_k ,
\]
and \( \theta_k \) is defined in eq. (i).

Employing a quantum Monte Carlo method\cite{3,4,5} we have calculated the thus-defined static structure factors at various temperatures, which are shown in Fig. 1. Both structure factors \( S^\lambda(k) \) have their peaks at \( k = 0 \), which reflects a combination of ferromagnetic and antiferromagnetic features in this system. However, they show quantitatively different temperature dependences. While the ferromagnetic peak is rapidly smeared out as the temperature increases, the antiferromagnetic one still persists at rather high temperatures. This observation implies that the antiferromagnetic correlation is dominant at intermediate temperatures and thus well explains the well-pronounced Schottky-like peak of the specific heat.

The existence of a gapped antiferromagnetic mode does not necessarily result in a Schottky-like behavior of the specific heat, which is basically inherent in two-level systems. As long as the specific heat shows a prominent peak reflecting the gap \( \Delta \), the lowest-lying antiferromagnetic mode should be fully stressed in the spectrum. In this context we inquire further into dynamic structure factors. We introduce the ferromagnetic and antiferromagnetic dynamic structure factors at \( T = 0 \) as
\[
S^{\pm}(k, \omega) = \sum_n \left| \langle n | S^- S^+ + S^+ S^- | 0 \rangle \right|^2 \delta (\omega - (E_n - E_0)) ,
\]
\[
S^{-}(k, \omega) = \sum_n \left| \langle n | S^- S^- + S^+ S^+ | 0 \rangle \right|^2 \delta (\omega - (E_n - E_0)) ,
\]
respectively, where \( S^\pm_k = S^\pm(0) \pm i S^\pm(0) \), \( S^\pm_k = S^\pm_k \pm i S^\pm_k \), \( | n \rangle \) denotes an eigenstate of the Hamiltonian (i) with energy \( E_n \), and \( E_0 \) is set to the ground-state energy. The ground states of quantum ferrimagnets are macroscopically degenerate and thus the choice for \( | 0 \rangle \) is not unique. We here assume the highest-magnetization ground state, namely, the lowest-energy state with \( M = (S-s)N \), as the initial state \( | 0 \rangle \) so that \( S^{-}(k, \omega) \) and \( S^{+}(k, \omega) \) can detect the ferromagnetic and antiferromagnetic elementary excitations, respectively. \( S^{\sigma}(k, \omega) \) \( (\sigma = \pm, \bar{\sigma} = -\sigma) \) is generally expressed in terms of its corresponding Green’s function as
\[
S^{\sigma}(k, \omega) = -\frac{1}{\pi} \text{Im} G^{\sigma}\bar{\sigma}(k, \omega) .
\]
\( G^{\sigma}\bar{\sigma}(k, \omega) \) is given as a continued fraction\cite{6,7}
\[
G^{\sigma}\bar{\sigma}(k, \omega) = \frac{| 0 \rangle S^\sigma S^-_{k0} | 0 \rangle}{\omega - a_0 - b^\sigma_k \sqrt{\omega - \omega - a_0 \mp \lambda \bar{\sigma}}} ,
\]
where the coefficients \( a_n \) and \( b_n \) are obtained by the Lanczos method through a recursive relation
\[
| f_{n+1} \rangle = \mathcal{H} | f_n \rangle - a_n | f_n \rangle - b^\sigma_n f_{n-1} \rangle , \quad | f_0 \rangle = S^-_{k0} | 0 \rangle , \quad b_0 = 0 .
\]
with a set of orthogonal states \( \{| f_n \rangle \} \). This method works fairly well\cite{8,9} for the study of low-lying states.
of various one-dimensional magnets.

The thus-calculated dynamic structure factors are shown in Fig. 2. We find qualitatively the same behavior at all the chain lengths we treated and therefore the present observations may be regarded as the long-chain behavior. This is due to the considerably small correlation length$^{[35]}$ of the system. In effect, the antiferromagnetic gap $\Delta$ is 1.7594$J$, 1.7592$J$, and 1.7591$J$ at $N = 8$, $N = 10$, and $N = 12$, respectively, the values of which are almost seen to converge. The scattering intensity is remarkably large at the lower boundaries of the ferromagnetic and antiferromagnetic spectra at each $k$, as was expected. In particular the lowest-lying antiferromagnetic poles hold most of the antiferromagnetic scattering weight. They are never smeared out in the ferromagnetic spectra but are prominently present. As far as antiferromagnetic eigenvalues are concerned, we can in principle detect all of them in the subspace of $M = (S - s)N + 1$, and therefore, their lower boundary seems to form a split band separated from an upper continuum. Thus the low-energy structure is essentially described by these well-pronounced ferromagnetic and antiferromagnetic bands, which are almost parallel to each other and are separated by the gap $\Delta = 1.759J$. This explains the reason why the specific heat is well fitted to the simple Schottky form$^{[27]}$

$$\frac{C}{Nk_B} \propto \frac{\Delta^2}{2k_BT^2} \sech^2 \left( \frac{\Delta}{2k_BT} \right), \quad (15)$$

at intermediate and even higher temperatures.

In conclusion, we have numerically studied the low-energy structure of Heisenberg ferrimagnetic spin chains in an attempt to understand their novel thermal behavior$^{[30]}$. The two distinct static structure factors illustrate why the clear ferromagnetic-to-antiferromagnetic crossover is observed in the temperature dependence of the thermodynamic quantities. As the temperature increases, the ferromagnetic nature rapidly fades out, whereas the antiferromagnetic one persists up to higher temperatures. That is why the specific heat exhibits a well-pronounced Schottky-like peak and the susceptibility-temperature product shows an increasing behavior with temperature, in spite of the low-temperature ferromagnetic behavior. On the other hand, the dynamic structure factors clearly indicate that the present model effectively behaves as a two-level system unless the temperature is sufficiently low. The findings will motivate further experimental study on this topic.

The authors would like to thank N. Fujiwara and M. Hagiwara for their useful comments. This work was supported by the Japanese Ministry of Education, Science, and Culture through a Grant-in-Aid (No. 09740286) and by the Okayama Foundation for Science and Technology.

Part of the numerical computation was carried out using the facility of the Supercomputer Center, Institute for Solid State Physics, University of Tokyo.

[1] T. Tonegawa, T. Hikihara, M. Kaburagi, T. Nishino, S. Miyashita and H.-J. Mikeska: J. Phys. Soc. Jpn. 67 (1998) 1000.
[2] T. Fukui and N. Kawakami: Phys. Rev. B 55 (1997) 14709; ibid. 56 (1997) 8799.
[3] T. Fukui and N. Kawakami: Phys. Rev. B 57 (1998) 308.
[4] A. Koga, S. Kumada, N. Kawakami and T. Fukui: J. Phys. Soc. Jpn. 67 (1998) 627.
[5] K. Takano: preprint [cond-mat/9804057].
[6] F. C. Alcaraz and A. L. Malvezzi: J. Phys. A 30 (1997) 767.
[7] S. K. Pati, S. Ramasesha and D. Sen: Phys. Rev. B 55 (1997) 8894; J. Phys.: Condens. Matter 9 (1997) 8707.
[8] A. K. Kolezhuk, H.-J. Mikeska and S. Yamamoto: Phys. Rev. B 55 (1997) 3336.
[9] S. Brehmer, H.-J. Mikeska and S. Yamamoto: J. Phys.: Condens. Matter 9 (1997) 3921.
[10] H. Niggemann, G. Uimim and J. Zittartz: J. Phys.: Condens. Matter 9 (1997) 9031; preprint [cond-mat/9712202].
[11] S. Yamamoto: Int. J. Mod. Phys. C 8, 609 (1997); S. Yamamoto, S. Brehmer and H.-J. Mikeska: Phys. Rev. B 57 (1998) 13610.
[12] T. Ono, T. Nishimura, M. Katsumura, T. Morita and M. Sugimoto: J. Phys. Soc. Jpn. 66 (1997) 2576.
[13] T. Kuramoto: J. Phys. Soc. Jpn. 67 (1998) 1762.
[14] S. Yamamoto and T. Fukui: Phys. Rev. B 57 (1998) 14008; S. Yamamoto, T. Fukui, K. Maisinger and U. Schollwöck: to be published in J. Phys.: Condens. Matter [cond-mat/9806344].
[15] N. B. Ivanov: Phys. Rev. B 57 (1998) 14024; N. B. Ivanov, J. Richter and U. Schollwöck: preprint [cond-mat/9803150].
[16] K. Maisinger, U. Schollwöck, S. Brehmer, H.-J. Mikeska and S. Yamamoto: Phys. Rev. B 58, No. 10 (1998).
[17] O. Kahn, Y. Pei and Y. Journoux: in Inorganic Materials, ed. D. W. Bruce and D. O’Hare (Wiley, New York, 1992) p. 95.
[18] M. Drillon, J. C. Gianduzzo and R. Georges: J. Phys. 96A (1983) 413; M. Drillon, E. Coronado, R. Georges, J. C. Gianduzzo and J. Curely: Phys. Rev. B 40 (1989) 16992.
[19] N. Fujiwara and M. Hagiwara: private communication.
[20] E. Lieb and D. Mattis: J. Math. Phys. 3 (1962) 749.
[21] F. D. M. Haldane: Phys. Lett. 93A (1983) 46; Phys. Rev. Lett. 50 (1983) 1153.
[22] S. Yamamoto: Phys. Rev. B 53 (1996) 3364.
[23] E. R. Gagliano and C. A. Balseiro: Phys. Rev. Lett. 50 (1983) 2999.
[24] S. Haas, J. Riera and E. Dagotto: Phys. Rev. B 48 (1993) 3281.
[25] M. Takahashi: Phys. Rev. B 50 (1994) 3045.
[26] M. Hagiwara, K. Minami, Y. Narumi, K. Tatani and K. Kindo: J. Phys. Soc. Jpn. 67 (1998) 2209.

Fig. 1. Ferromagnetic (a) and antiferromagnetic (b) static structure factors as functions of temperature for the chain of $N = 32$. The temperature is indicated in units of $J/k_B$ in the inset.

Fig. 2. Ferromagnetic ($\times$) and antiferromagnetic (+) dynamic structure factors at the absolute zero temperature. The lowest-energy five poles are shown for each of them. The intensity of each pole is proportional to the area of the circle.
Fig. 1(a) S. Yamamoto and T. Sakai
Fig. 1(b) S. Yamamoto and T. Sakai
Fig. 2(a)  S. Yamamoto and T. Sakai
Fig. 2(b) S. Yamamoto and T. Sakai

(b) $N = 10$
Fig. 2(c) S. Yamamoto and T. Sakai

\[ \frac{\omega}{J} = 12 \]