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Thermodynamic Properties of the Transverse-Crystal-Field
Ising Model on a $\Delta$ Chain

--- Three Peak Structure in the Specific Heat ---

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The specific heat of the $S = 1$ transverse-crystal-field Ising model with an antiferromagnetic exchange interaction $J$ on a $\Delta$-chain is studied by using the exact-diagonalization, quantum Monte Carlo and finite-temperature Lanczos methods. We find that when the strength of the transverse crystal field $\Gamma$ is chosen to be sufficiently small, the specific heat exhibits a three-peak structure as a function of temperature, with peaks at $T \sim 0.05\Gamma$, $0.2\Gamma$ and $0.7J$. In addition to the two energy scales $\Gamma$ and $J$, a new energy scale $\sim 0.1 \times \Gamma$ appears due to the geometrical frustration and the existence of the $S^z = 0$ states in the present system.

§1. Introduction

Geometrically frustrated spin systems have attracted considerable attention for a long time. It is expected that the introduction of quantum fluctuations into a classically degenerate manifold leads to exotic properties of ground states and thermodynamics. From this point of view, $S = 1/2$ transverse-field Ising antiferromagnets on various geometrically frustrated lattices have recently been studied.1)–3)

The simplest frustrated one-dimensional lattice $\Delta$-chain, shown in Fig. 1, has been treated in such studies. The residual entropy of an $S = 1/2$ Ising antiferromagnet on a $\Delta$-chain constitutes 80% of the total entropy. It was shown by Priour et al. that transverse magnetic fields remove the ground state degeneracy without spontaneous symmetry breaking. They termed this the “disorder by disorder phenomenon”.2) With regard to systems with higher spin values, the present authors conducted a series expansion study of the ground state quantum phase transition in the $S = 1$ transverse-magnetic-field Ising model and found that small transverse magnetic fields stabilize an ordered state in which bottom spins are ordered antiferromagnetically and tip spins point in the direction of the transverse magnetic field.3) (This ordered state is termed a “staggered state” hereafter.)

It is well known that the single-ion anisotropy generated by the crystal fields plays an important role in real materials described by spin Hamiltonians with $S \geq 1$. Eddeqaqi et al. studied two-dimensional $S = 1$ Ising models with transverse crystal fields and searched for tricritical phenomena in their phase diagrams.4) Yamada et al. recently used an $S = 1$ transverse-crystal-field Ising model on a three-dimensional lattice to describe the ferroelectric transition in SrTiO$_3$ induced by isotope replacement.5)
Y. Fukumoto and A. Oguchi

Fig. 1. Schematic representation of the $\Delta$-chain. The solid lines represent the antiferromagnetic exchange coupling $J$, and the open circles denote spin sites.

In this paper, we treat an $S = 1$ Ising antiferromagnet on a $\Delta$ chain subject to transverse crystal fields described by the Hamiltonian

$$H = J \sum_{\langle i, j \rangle} S^z_i S^z_j - \Gamma \sum_i (S^x_i)^2, \quad (1.1)$$

where $\langle i, j \rangle$ denotes nearest neighbor pairs of sites on the $\Delta$ chain. We first note that the operator $(S^x_i)^2$ has a unique conservation property, which we now describe. We choose $z$ as the quantization axis and introduce a basis set $\{ |S^z_i\rangle; S^z = -1, 0, +1 \}$. Then the matrix representation of $(S^x_i)^2$ becomes

$$\begin{pmatrix}
1 & 0 & \frac{1}{2} \\
0 & 1 & 0 \\
\frac{1}{2} & 0 & \frac{1}{2}
\end{pmatrix}, \quad (1.2)$$

which contains no matrix element that changes the $S^z = 0$ state. Therefore, all $S^z = 0$ sites are conserved quantities in this Hamiltonian.

Oittma and Brasch proved that $S = 1$ transverse-crystal-field Ising models on arbitrary lattices possess no $S^z = 0$ sites in their ground states. Thus, $S^z = 0$ sites play no role at $T = 0$. In other words, the problem concerning the ground states of $S = 1$ transverse-crystal-field Ising models can be mapped to that of $S = 1/2$ transverse-magnetic-field Ising models. However, the existence of the $S^z = 0$ state might lead to interesting thermodynamic properties. Indeed, for the case of the $\Delta$ chain considered in this paper, a three-staged entropy release appears due to the existence of the $S^z = 0$ state.

This paper is organized as follows. In §2, the model given in Eq. (1.1) is generalized such that the crystal field experienced by the bottom spins can take different values from that experienced by the tip spins, and we study the ground state phase diagram for this generalized model. In §3, we prepare an exact diagonalization study for a small size cluster to obtain a physical picture of the thermodynamic properties. We develop a continuous time cluster algorithm for transverse-crystal-field Ising models in §4 and present data for the specific heat of the $\Delta$ chain model. In §5, the specific heat of the $\Delta$ chain model with an infinitesimal value of $\Gamma/J$ is calculated for finite size systems with up to 32 spins, and extrapolation is carried out to estimate the specific heat in the thermodynamic limit. The results obtained in this paper are summarized in §6.
§2. Ground state phase diagram for a generalized model

In order to obtain insight into the model given in Eq. (1.1), it is helpful to consider the following generalized model:

\[ H_{\lambda} = J \sum_{\langle i,j \rangle} S_i^z S_j^z - \Gamma \sum_{i \in \text{tip}} (S_i^x)^2 - \lambda \Gamma \sum_{i \in \text{bottom}} (S_i^x)^2. \]  

(2.1)

Here, in order to separate the crystal fields into those experienced by the tip and bottom spins, we introduce the factor \( \lambda \geq 0 \) in the crystal field term for the bottom spins. In this section, we investigate the ground state phase diagram of this generalized model.

Oittma and Brasch’s theorem holds for \( H_{\lambda} \) if the crystal fields are applied to all of the sites. Thus, the ground state of \( H_{\lambda} \) belongs to the sector without \( S^z = 0 \) sites for \( \Gamma \neq 0 \) and \( \lambda > 0 \). In order to obtain a Hamiltonian describing the subspace without \( S^z = 0 \) sites, we take

\[ S_i^z \rightarrow \sigma_i^z, \quad (S_i^x)^2 \rightarrow \frac{1}{2}(1 + \sigma_i^x), \]  

(2.2)

where \( \sigma_i^z \) and \( \sigma_i^x \) denote the \( S = 1/2 \) Pauli operators. Then we obtain

\[ H^0_{\lambda} = J \sum_{\langle i,j \rangle} \sigma_i^z \sigma_j^z - \frac{\Gamma}{2} \sum_{i \in \text{tip}} \sigma_i^x - \frac{\lambda \Gamma}{2} \sum_{i \in \text{bottom}} \sigma_i^x - \frac{1}{4} \lambda L \Gamma (1 + \lambda), \]  

(2.3)

where \( L \) denotes the total number of spins.

The Hamiltonian \( H^0_{\lambda} \) is that of the ordinary \( S = 1/2 \) transverse-field Ising model. The present authors studied the ground state phase diagram of this model and found that two phases — the transverse-field paramagnetic phase and the staggered phase — appear in the \( \lambda-\Gamma \) plane. Using these results, we can immediately obtain the transition line between the two phases of the \( S = 1 \) transverse crystal-field Ising model. The result is shown in Fig. 2. The eigenvalue distribution for the Hamiltonian of the original model, \( H_{\lambda} \), is not symmetric under \( \Gamma \leftrightarrow -\Gamma \). However, the transition line is symmetric because the line is determined in the sector described by the \( S = 1/2 \) transverse-field Ising model, \( H^0_{\lambda} \). In the limit \( \Gamma/J \rightarrow \pm 0 \), the critical value of \( \lambda \) is 0.9459. The transverse field paramagnetic phase is stabilized on the uniform crystal field line, \( \lambda = 1 \), which implies that the \( S = 1 \) transverse crystal field Ising model \( H (= H_{\lambda = 1}) \) yields an example of disorder by disorder phenomena similar to that in the \( S = 1/2 \) transverse magnetic field Ising model.

Oittma and Brasch’s theorem does not apply to the case in which \( \Gamma = 0 \) or \( \lambda = 0 \). For \( \Gamma = 0 \), the case in which no transverse crystal fields are applied, all configurations minimizing the exchange energy form the ground state manifold. The existence of this manifold results in a residual entropy of \( S(T = 0)/L \simeq 0.75 \). For \( \lambda = 0 \) and \( \Gamma \neq 0 \), the case in which transverse crystal fields are experienced only by the tip spins, we can solve the model exactly. The temperature dependence

\( ^1 \) Because the tip spins are not connected directly each other by the exchange coupling, we can take the trace concerned with the tip spins. Thermodynamic quantities of the resultant “classical” system can be calculated by the transfer matrix method.
Fig. 2. Ground state phase diagram for the generalized model $H_\lambda$. In the graphical representations of the spin configurations, the longitudinal arrows represent $|S^z = +1\rangle$ or $|S^z = -1\rangle$ and the horizontal arrows represent $\frac{1}{\sqrt{2}}(|S^z = 1\rangle \pm |S^z = -1\rangle)$, which implies that the effective spin 1/2 operator introduced in Eq. (2.2) points in the $\pm x$ directions. There exists residual entropy for systems on the thick gray lines.

Fig. 3. Temperature dependence of the entropy for systems with $\Gamma/J = \pm 0.2$, $\lambda = 0$ and $L = \infty$. The horizontal dotted lines indicate the characteristic values of the entropy: $S/L = \log 3 \simeq 1.1$ is that associated with the total number of all states, $S/L \simeq 0.75$ is that associated with the total number of states minimizing the exchange energy, and $S/L = \log \sqrt{2} \simeq 0.35$ is that associated with the degrees of freedom of tip spins.

of entropy for $\lambda = 0$ and $\Gamma/J = \pm 0.2$ is depicted in Fig. 3. We find that there is a residual entropy of $S(T = 0)/L = \log \sqrt{2} \simeq 0.35$ for $\Gamma/J = +0.2$. In this case, the crystal fields with $\Gamma > 0$ experienced by the tip spins fix the bottom spin configuration. However, each tip spin has two choices for its ground state, i.e., $|S^z = 0\rangle$ and $(|S^z = 1\rangle + |S^z = -1\rangle)/\sqrt{2}$. Contrastingly, the ground state for $\Gamma/J = -0.2$ is uniquely determined by the crystal fields experienced by tip spins. The gray thick lines in Fig. 2 represent fully frustrated lines, which exist for $\Gamma = 0$ and $\lambda = 0$ with $\Gamma > 0$.

As asserted by Oittma and Brasch’s theorem, $S^z = 0$ sites play no role in the ground state if $\Gamma \neq 0$ and $\lambda > 0$. However, the fully frustrated line corresponding to $\lambda = 0$ with $\Gamma > 0$ appears in the ground state phase diagram, and there exist $S^z = 0$
sites in states in the ground state manifold on that line. Hence, it is interesting to study how the existence of $S_z = 0$ sites affects the thermodynamic properties of $H (= H_{\lambda=1})$. We calculate the specific heat for $H$ in the following sections.

§3. Exact diagonalization

In this section, we perform exact calculations for a small cluster with $L = 12$ in order to study the thermodynamic properties of the model $H$ in Eq. (1.1) qualitatively.

The calculated results for the specific heat per spin are shown in Fig. 4. We find in Fig. 4(a) that a three-peak structure is observed for $\Gamma > 0$: The lowest temperature peak is at $T \sim 0.05\Gamma$, the second lowest temperature peak at $T \sim 0.2\Gamma$, and the highest temperature peak at $T \sim 0.7J(\sim \infty \times \Gamma$, $4\Gamma$, $2\Gamma$) for $\Gamma/J = +0$, $+0.2$, $+0.4$, $+0.5$). We also observe that the valley between the lowest and second lowest temperature peaks becomes deeper as $\Gamma/J$ decreases. By contrast, for $\Gamma < 0$ depicted in Fig. 4(b), we observe only two peaks, at $T \sim 0.4|\Gamma|$ and $T \sim 0.7J$. (The small peak or shoulder around $T/|\Gamma| \sim 0.03$ appears due to finite size effects.)

The three-peak structure for $\Gamma > 0$ reflects the existence of the fully frustrated line for $\lambda = 0$ with $\Gamma > 0$ shown in Fig. 2. In order to investigate this further, we plot the specific heat of the generalized model $H_\lambda$ for $\Gamma/J = +0$ and several values of $\lambda$ in Fig. 5. (It should be noted that the highest temperature peak resulting from the exchange interaction is located at $T/\Gamma = \infty$, and thus, it is not shown in the figure.) As expected, the peak position of the lowest temperature peak decreases when we decrease $\lambda$. The inset displays the $\lambda$ dependence of the peak positions. We can confirm from the inset that the peak temperature of the lowest temperature peak tends to zero as the crystal field on the bottom spins goes to zero.

It is also useful to study the $\lambda$ dependence of the energy histogram $N(E)$ to
gain an understanding of the behavior of the specific heat. The calculated results are plotted in Fig. 6, where the size of the energy discretization for the histogram is chosen as 0.1Γ. In the figure, the thin line is the histogram for all sectors, and the thick line is that for the sectors in which there are \( S^z = 0 \) sites only at tip spin sites. At \( \lambda = 0.8 \) in Fig. 6(a) and \( \lambda = 1.0 \) in Fig. 6(b), we find that there exists a low energy weight (the shadowed region in the figure) that is separated from the other part. This feature in the energy histogram yields a two-peak structure of the specific heat for \( \lambda = 0.8 \) and 1.0 in Fig. 5. Contrastingly, we cannot find such well separated low energy weight at \( \lambda = 1.2 \) in Fig. 6(c), and the two-peak structure collapses there, as seen in Fig. 5.

The states in the shadowed region in Figs. 6(a) and 6(b) originate from states in the ground state manifold at \( \lambda = 0 \). From Fig. 6(b) for \( \lambda = 1 \), we find that the total bandwidth is 6.9Γ and the upper edge of the shadowed region is at 0.5Γ. This implies that we have a new energy scale, \( (0.5/6.9) \Gamma \sim 0.1\Gamma \), in addition to the two energy scales \( \Gamma \) and \( J \), which are contained explicitly in the model Hamiltonian \( H \).

§4. Quantum Monte-Carlo simulation

In the previous section, we found that the specific heat of a small system described by \( H \) with \( \Gamma > 0 \) exhibits a three-peak structure. However, there remains the question of whether such a structure also exists in the thermodynamic limit. In this and the next section, we study the dependence of the specific heat on the system size in an attempt to answer this question. Here we formulate the algorithm for the Monte Carlo simulation for \( S = 1 \) transverse-crystal-field Ising models, and apply it to the \( \Delta \) chain model. A continuous time cluster algorithm for \( S = 1/2 \) transverse-field Ising models was developed by Rieger and Kawashima.\textsuperscript{8) We modified their

\textsuperscript{8} If a system with \( L \) spins has two energy scales, \( \Gamma \) and \( a\Gamma \) \( (a \ll 1) \), then we expect that the total band width, \( \Delta W_{\text{tot}} \), is written as \( \Delta W_{\text{tot}} \sim \Gamma L \) and the width of a band concerning low energy dynamics, \( \Delta W_{\text{led}} \), is written as \( \Delta W_{\text{led}} \sim a\Gamma L \). Using \( \Delta W_{\text{tot}} \) and \( \Delta W_{\text{led}} \), we can express the second energy scale as \( a\Gamma \sim (\Delta W_{\text{led}}/\Delta W_{\text{tot}})\Gamma \).
Thermodynamic Properties of the $\Delta$-Chain Transverse-Field Ising Model

Fig. 6. Energy histogram $N(E)$ for $\Gamma/J = +0$ with (a) $\lambda = 0.8$, (b) $\lambda = 1.0$, and (c) $\lambda = 1.2$, where the size of the energy discretization is chosen as $0.1\Gamma$ and the energy is measured from the ground state energy $E_g$. The thin line is the histogram for all sectors, and the thick line is the histogram for the sectors containing $S^z = 0$ sites only at tip spin sites. The states in the shadowed part in (a) and (b) originate from those in the ground state manifold at $\lambda = 0$.

Following Harada et al. and Todo and Kato, we divide each $S = 1$ operator into two $S = 1/2$ operators:

$$S_l \rightarrow \frac{1}{2} \sum_{\mu=1}^{2} \sigma_{l,\mu}. \hspace{1cm} (4.1)$$

By substituting this into the original Hamiltonian $H$, we obtain

$$\tilde{H} = \tilde{H}_1 + \tilde{H}_2, \hspace{1cm} (4.2)$$

where

$$\tilde{H}_1 = \frac{J}{4} \sum_{(l,m)} \sum_{\mu,\nu} \sigma_{l,\mu}^z \sigma_{m,\nu}^z, \hspace{0.5cm} \tilde{H}_2 = -\frac{\Gamma}{2} \sum_{l} \sigma_{l,1}^x \sigma_{l,2}^x. \hspace{1cm} (4.3)$$
The partition function \( Z \) for \( H \) is written in terms of \( \tilde{H} \) as

\[
Z = \text{Tr} e^{-\beta \tilde{H}} \prod_l P_l,
\]

where

\[
P_l = \frac{1}{4} (3 + \sigma_{l,1} \cdot \sigma_{l,2})
\]

is the projection operator which eliminates the unphysical singlet pair state at the \( l \)th site.

Using the Suzuki-Trotter decomposition,

\[
e^{-\beta (H_1 + H_2)} = \left( e^{-\frac{1}{n} \beta H_1} e^{-\frac{1}{n} \beta H_2} \right)^n \quad \text{for } n \to \infty,
\]

to express the partition function \( Z \) in terms of local Boltzmann weights, we get

\[
Z = \sum_{\{\sigma\}} W_s(\{\sigma\}) W_t(\{\sigma\}) W_b(\{\sigma\}),
\]

where

\[
W_s(\{\sigma\}) = \prod_{l,m} \prod_{\mu,\nu} \prod_{q=1}^n w_s(\sigma_{l,\mu}^{(q)}, \sigma_{m,\nu}^{(q)}; \beta),
\]  
\[
W_t(\{\sigma\}) = \prod_{l} \prod_{q=1}^n w_t(\sigma_{l,1}^{(q)}, \sigma_{l,2}^{(q)}, \sigma_{l,1}^{(q+1)}, \sigma_{l,2}^{(q+1)}; \beta),
\]  
\[
W_b(\{\sigma\}) = \prod_{l} w_b(\sigma_{l,1}^{(n+1)}, \sigma_{l,2}^{(n+1)}, \sigma_{l,1}^{(1)}, \sigma_{l,2}^{(1)}; \beta).
\]

Explicit expressions for \( w_s, w_t \) and \( w_b \) are given as follows:

\[
w_s(\sigma_{l,\mu}^{(q)}, \sigma_{m,\nu}^{(q)}; \beta) = \exp \left[ -\frac{\beta J}{4n} \sigma_{l,\mu}^{(q)} \sigma_{m,\nu}^{(q)} \right],
\]  
\[
w_t(\sigma_{l,1}^{(q)}, \sigma_{l,2}^{(q)}, \sigma_{l,1}^{(q+1)}, \sigma_{l,2}^{(q+1)}; \beta) = \cosh \left( \frac{\beta \Gamma}{2n} \right) \langle \sigma_{l,1}^{(q)}, \sigma_{l,2}^{(q)} | \sigma_{l,1}^{(q+1)}, \sigma_{l,2}^{(q+1)} \rangle
\]
\[
+ \sinh \left( \frac{\beta \Gamma}{2n} \right) \langle \sigma_{l,1}^{(q)}, \sigma_{l,2}^{(q)} | \sigma_{l,1}^{(q+1)}, \sigma_{l,2}^{(q+1)} \rangle \langle \sigma_{l,1}^{(1)}, \sigma_{l,2}^{(1)} | (3 + \sigma_{l,1} \cdot \sigma_{l,2}) | \sigma_{l,1}^{(1)}, \sigma_{l,2}^{(1)} \rangle.
\]  
\[
w_b(\sigma_{l,1}^{(n+1)}, \sigma_{l,2}^{(n+1)}, \sigma_{l,1}^{(1)}, \sigma_{l,2}^{(1)}; \beta) = \frac{1}{4} (\sigma_{l,1}^{(n+1)} | 3 + \sigma_{l,1} \cdot \sigma_{l,2} | \sigma_{l,1}^{(1)} 
\]

In order to construct the clusters to be flipped randomly, we apply the algorithm developed by Swendsen and Wang\(^\text{11}\) or its generalized version developed by Kandel and Domany.\(^\text{12}\) We now describe the rule for the assignment of links which defines the clusters under the local Boltzmann weights obtained above. For a spin pair \((\sigma_{l,\mu}^{(q)}, \sigma_{m,\nu}^{(q)})\) connected by the antiferromagnetic interaction, if these two spins are antiparallel, then we put a link between them with probability \(1 - e^{-\beta J/2n}\).\(^\text{11}\) For plaquettes \((\sigma_{l,1}^{(q)}, \sigma_{l,2}^{(q)}, \sigma_{l,1}^{(q+1)}, \sigma_{l,2}^{(q+1)})\) with \(q = 1, \ldots, n\), possible link configurations
Fig. 7. Possible link configurations for plaquettes \((\sigma_{l,1}^{(q)}, \sigma_{l,2}^{(q)}, \sigma_{l,1}^{(q+1)}, \sigma_{l,2}^{(q+1)})\) with \(q = 1, \ldots, n\). The direction of spins represented by closed circles is opposite that of spins represented by open circles. The solid lines represent links. The probabilities to accept the various link configurations are \(1 - \tanh(\beta \Gamma/2n)\) for (a), \(\alpha \tanh(\beta \Gamma/2n)\) for (b), \((1 - \alpha) \tanh(\beta \Gamma/2n)\) for (c), \(\alpha\) for (d), and \(1 - \alpha\) for (e).

The direction of spins represented by closed circles is opposite that of spins represented by open circles. The solid lines represent links. The probabilities to accept the various link configurations are \(1 - \tanh(\beta \Gamma/2n)\) for (a), \(\alpha \tanh(\beta \Gamma/2n)\) for (b), \((1 - \alpha) \tanh(\beta \Gamma/2n)\) for (c), \(\alpha\) for (d), and \(1 - \alpha\) for (e).

are summarized in Fig. 7. If the spin states are unchanged along the time direction, i.e., we have \(\sigma_{l,1}^{(q)} = \sigma_{l,1}^{(q+1)}\) and \(\sigma_{l,2}^{(q)} = \sigma_{l,2}^{(q+1)}\), then we put a pair of straight links along the time direction with probability \(1 - \tanh(\beta \Gamma/2n)\). If this link assignment is rejected or spin states change along the time direction, we put a pair of straight links along the space direction with probability \(\alpha \in (0, 1]\), where we can choose \(\alpha\) arbitrarily and use it as a tuning parameter. If this link assignment is not accepted, then we put crossing links. For a plaquette at the boundary, \((\sigma_{l,1}^{(n+1)}, \sigma_{l,2}^{(n+1)}, \sigma_{l,1}^{(1)}, \sigma_{l,2}^{(1)})\), straight links along the time direction or crossing links are chosen in order to connect the spins pointing in the same direction. If both types of link configurations are possible, then we choose one of them at random\(^9,10\) [see Fig. 1 in Ref. 9].

On the basis of the algorithm described above for link assignments, it is possible to take the \(n \to \infty\) limit to derive a continuous time algorithm, as done by Rieger and Kawashima.\(^8\) The procedure for updating the spin configuration in the continuous time limit is summarized in Fig. 8. An old configuration before updating is depicted in Fig. 8(a). At each site, there exist two world lines, \(\sigma_{l,1}^{(\tau)}\) and \(\sigma_{l,2}^{(\tau)}\). The solid and dashed lines represent world line segments with spin up and down, respectively. In order to construct the clusters, first, we add new cuts (the horizontal dashed lines) in addition to old cuts (the horizontal solid lines), as shown in Fig. 8(b). Old segments are divided by new cuts, and the length of the divided segment \(t\) is determined stochastically by the Poisson distribution \(e^{-\frac{1}{2}\beta \Gamma t}\). Then we insert crossing links or horizontal links in each cut with the probabilities \(\alpha\) and \(1 - \alpha\) and put appropriate links at the boundaries, as shown in Fig. 8(c). Next, as shown in Fig. 8(d), we put horizontal links between antiparallel segments on two different sites connected by the exchange interaction with probability \(1 - e^{-\frac{1}{2}\beta J \Delta t}\), where \(\Delta t\) is the time overlap of the antiparallel segments. The numbers in this figure represent the indices for independent clusters. The independent clusters are flipped randomly, as shown in Fig. 8(e). By removing all links used to specify the cluster configuration, we obtain a new spin configuration [see Fig. 8(f)].

In order to test this algorithm, we calculated the specific heat for a small sys-

\(^{9}\) It should be noted that ergodicity does not hold at \(\alpha = 0\), although the detailed balance condition is satisfied for \(0 \leq \alpha \leq 1\). We chose \(\alpha = 1/2\) in the calculations reported in the paper.
system with $L = 12$. From this investigation, we found that the performance is not satisfactory: Although the highest temperature peak originating from the exchange interaction is reproduced, we could not obtain the other two peaks, originating from the transverse crystal field. As stated above, $S^z = 0$ sites are conserved quantities in this model. At high temperatures, various configurations of $S^z = 0$ sites appear during the simulation. However, at lower temperatures, the $S^z = 0$ site configuration rarely changes. It seems that the appearance of energy barriers between different $S^z$ site configurations is the reason behind the poor performance of the simulation.

We intend to incorporate an exchange process into the simulation to overcome this problem. The exchange Monte Carlo method was originally developed by Hukushima and Nemoto to overcome the problem of the long relaxation time in the low temperature phase of spin glasses. In this method, simulations at several temperatures are performed simultaneously, and the spin configurations at different temperatures are interchanged during the simulations. The probability for the interchange of $\{\sigma\}$ at an inverse temperature $\beta$ and $\{\bar{\sigma}\}$ at $\bar{\beta}$ is given by

$$P(\{\sigma\}, \beta|\{\bar{\sigma}\}, \bar{\beta}) = \begin{cases} 1 & \text{for } \epsilon < 0, \\ e^{-\epsilon} & \text{for } \epsilon > 0. \end{cases}$$ (4.10)
Here, $\epsilon$ is defined by

$$\epsilon = \frac{\bar{\beta} - \beta}{4} \sum_{\langle l,m \rangle} \sum_{\nu,\mu} \int_0^1 d\tau [\sigma^{(\tau)}_{l\nu} \sigma^{(\tau)}_{m\mu} - \bar{\sigma}^{(\tau)}_{l\nu} \bar{\sigma}^{(\tau)}_{m\mu}] - \log \left( \frac{\bar{\beta}}{\beta} \right) \times \sum_{l} \int_0^1 d\tau \left[ \sum_{l} \delta(\tau - \tau_{\text{cut}}^{(l)}) - \sum_{l} \delta(\tau - \bar{\tau}_{\text{cut}}^{(l)}) \right],$$

(4.11)

where $\tau_{\text{cut}}^{(l)}$ represents the times at which the values of $(\sigma_{l1}^{(\tau)}, \sigma_{l2}^{(\tau)})$ change.

In order to test the performance of the exchange Monte Carlo algorithm, we calculated the specific heat at $\Gamma/J = 0.4$ for an $L = 12$ cluster, where the temperature range is chosen as $0.5 \leq J\beta \leq 25$ and the size of the temperature discretization is chosen as $\delta(J\beta) = 24.5/30$. We carried out 6 simulations with $2 \times 10^6$ Monte Carlo steps. In Fig. 9, we compare the result obtained with the exchange Monte Carlo algorithm (denoted by the cross) and the exact result (denoted by the solid line). The error bars are estimated from the standard deviation over the 6 runs. It is seen that the two results are in good agreement within the calculated temperature range. However, we could not succeed in reproducing the lowest temperature peak, because of the long relaxation time at very low temperatures.

In order to study the manner in which the valley between the lowest and second lowest temperature peaks changes as the system size increases, we calculated the specific heat for larger clusters. The results for clusters with $L = 16$, 24 and 32 are also shown in Fig. 9. We observe that the valley tends to collapse when the system size increases, suggesting that the second lowest temperature peak observed for small clusters changes to a shoulder in the thermodynamic limit for $\Gamma/J = 0.4$.

As found in the exact diagonalization study, the valley between the lowest
and second lowest temperature peaks becomes deeper when \( \Gamma/J \) is decreased [see Fig. 4(a)]. Therefore, it would be interesting to study the specific heat in thermodynamic limit for smaller values of \( \Gamma/J \). However, such a study requires calculations at lower temperatures, which is clearly beyond the capability of the present Monte Carlo simulation. For this reason, we employed the finite-temperature Lanczos method to calculate the specific heat at \( \Gamma/J = +0 \) in thermodynamic limit instead of the Monte Carlo method. Our results are reported in the next section.

§5. Finite temperature Lanczos method

A numerical approach for calculating an eigenvalue distribution function was developed by Otsuka,\textsuperscript{14}) and it was successfully used to obtain the specific heat for a Heisenberg antiferromagnet on a \( \Delta \) chain up to \( L = 26 \). Here, we apply this method to calculate the specific heat for \( H \) given in Eq. (1.1) with \( \Gamma/J = +0 \) on clusters up to \( L = 32 \).

As stated in §1, \( S^z = 0 \) site configurations are conserved quantities in the transverse-crystal-field Ising model. Thus, it is convenient to calculate the eigenvalue distribution function for each sector specified by the \( S^z = 0 \) site configuration and then sum up the results to obtain the total eigenvalue distribution function for \( H \). Since the total number of \( S^z = 0 \) site configurations increases exponentially as the system size \( L \) grows, it is expected that the total number of eigenvalue distribution functions is much too large to be treated fully. However, as long as we concentrate on the limit \( \Gamma/J \rightarrow +0 \), the situation is significantly simplified, as described below.

In order to calculate the specific heat for \( T \simeq \Gamma \) in the case of \( H \) with \( J/\Gamma = \infty \), we construct a first-order effective Hamiltonian in \( \Gamma \) for the subspace with the minimum exchange energy.

We begin with the one-triangle problem with the 27 spin configurations shown in Fig. 10. The minimum exchange energy is realized for the 12 configurations depicted in (a) and (c). We also note that the triangle configurations with two or more \( S^z = 0 \) sites in (e) and (f) possess a higher exchange energy, and the spin flip caused by the transverse crystal field term makes the minimum exchange energy configurations in (c) change to the higher exchange energy configurations in (d).

Taking these facts into account, we can write an effective Hamiltonian in the

\[
E_\Delta = -J \quad 3J \quad -J \quad J \quad 0 \quad 0
\]

Fig. 10. Possible spin configurations for the one-triangle problem. The up and down arrows and open circles represent \(|S^z = +1\rangle\), \(|S^z = -1\rangle\) and \(|S^z = 0\rangle\), respectively. The number appearing in each triangle is the number of different configurations that are generated by the rotation and/or spin inversion operations, and \(E_\Delta\) denotes the exchange energy.
subspace with the minimum exchange energy as follows:

\[ H_{\text{eff}} = \Gamma \sum_{\mu \in \mathcal{M}} \sum_{l, l' \in \mathcal{L}_\mu} \langle l, \mu | V_\mu | l', \mu \rangle \langle l', \mu |. \]  

(5.1)

Here, we have written the \( S^z \) basis set as \( \{ |l, \mu \rangle \} \), where \( \mu \) indicates the \( S^z = 0 \) site configuration and \( l \) indicates the possible spin configuration for a fixed \( S^z = 0 \) site configuration \( \mu \). Also, \( \mathcal{M} \) represents the set of \( S^z = 0 \) site configurations for which no triangle contains two or more \( S^z = 0 \) sites, and \( \mathcal{L}_\mu \) represents the set of spin configurations with the minimum exchange energy. The operator \( V_\mu \) is defined by

\[ V_\mu = -\frac{1}{2} \sum_{i \in s_\mu} \sigma^x_i - \frac{1}{2} L_\mu, \]  

(5.2)

where \( s_\mu \) is the set of sites that are not on triangles containing \( S^z = 0 \) sites (see Fig. 11 for an example), \( L_\mu \) is the total number of \( S^z = 0 \) sites, and the Pauli operator \( \sigma^x_i \) satisfies \( \sigma^x_i | S^z = \pm 1 \rangle_i = | S^z = \mp 1 \rangle_i \). It should be noted that the spin state of a site next to a \( S^z = 0 \) site is fixed in this effective Hamiltonian, because any change in the spin state leads to an increase in the exchange energy. As seen in Fig. 11, \( S^z = 0 \) sites divide the system into successive spin segments that can be flipped. Each of the segments forms an open \( \Delta \) chain with fixed edge spins. We can calculate the energy eigenvalues of a segment by using both the Hamiltonian, \(-\frac{1}{2} \sum_{i \in \text{segment}} \sigma^x_i\), and the information regarding the edge spin state, which determines the constrained Hilbert space for the segment. We write the eigenvalue distribution function of a segment with \( n_t \) triangles as \( \rho_{n_t, \sigma \sigma'}(\omega) \), where \( (\sigma, \sigma') \) is the edge spin state. [If \( \mu \) contains no \( S^z = 0 \) sites, then the segment becomes a periodic \( \Delta \) chain, and we denote the eigenvalue distribution function as \( \rho_{n_t}(\omega) \).]

Therefore, the calculation of the eigenvalue distribution function for the \( S = 1 \) transverse-crystal-field Ising model on a periodic \( \Delta \) chain with \( L \) spins, \( \rho^{(\text{cf})}_{L/2}(\omega) \), is reduced to the calculation of \( L - 1 \) eigenvalue distribution functions for \( S = 1/2 \) systems \( \{ \rho_{1, \uparrow \uparrow}, \rho_{1, \uparrow \downarrow}, \cdots, \rho_{L/2-1, \uparrow \downarrow}, \rho_{L/2-1, \uparrow \uparrow}, \rho_{L/2} \} \). The construction of the relation between \( \rho^{(\text{cf})}_{L/2} \) and \( \{ \rho_{1, \uparrow \uparrow}, \cdots \} \) is straightforward. For example, we find the following relation for the \( L = 8 \) system:

\[ \rho^{(\text{cf})}_{4}(\omega) = 8\delta(\omega + 1) + 8\delta(\omega + 3/2) + 2\delta(\omega + 2) + 16\rho_{1, \uparrow \uparrow}(\omega + 1) + 16\rho_{1, \uparrow \downarrow}(\omega + 1) + 8\rho_{1, \uparrow \uparrow}(\omega + 3/2) + 8\rho_{2, \uparrow \downarrow}(\omega + 1/2) + 8\rho_{1, \uparrow \downarrow}(\omega + 1) + 8\rho_{2, \uparrow \downarrow}(\omega + 1/2) \]

Fig. 11. An example of the set of sites \( s_\mu \). The open circles represent \( S^z = 0 \) sites, and the closed circles represent the sites belonging to \( s_\mu \).
where we have chosen $\Gamma$ as the unit of $\omega$. For larger systems, we have constructed similar expressions by computer.

We now give a brief review of Otsuka’s method used to calculate the eigenvalue distribution functions of $S = 1/2$ systems. The eigenvalue distribution function, $\rho(\omega)$, can be written as

$$\rho(\omega) = -\frac{1}{\pi} \sum_{q=1}^{N_{\text{dim}}} \text{Im} G_{q,q}(\omega + i\eta), \quad (5.4)$$

where $q$ is the index of the basis set, $N_{\text{dim}}$ is the total number of basis elements, $\eta$ an infinitesimal positive number, and $G_{q,q}$ a matrix element of the Green function defined by

$$G_{q,q}(z) = \langle q | \frac{1}{z - H} | q \rangle, \quad (5.5)$$

where $H$ is the Hamiltonian under consideration. Generally, $N_{\text{dim}}$ is too large to carry out the summation in Eq. (5.4) completely, and therefore we have to employ a sampling technique. Generating a set of normalized random vectors, $\{\phi_j | j = 1, \cdots, n_{\text{dim}}\}$, where $n_{\text{dim}}$ is chosen to be $\sim O(10)$ to $O(1000)$, we make the approximation

$$\rho(\omega) \simeq -\frac{C}{\pi} \sum_{j=1}^{n_{\text{dim}}} \text{Im} G_{\phi_j,\phi_j}(\omega + i\eta), \quad (5.6)$$

where $C$ is determined by the condition $\int d\omega \rho(\omega) = N_{\text{dim}}$. In order to calculate $G_{\phi,\phi}$, we utilize the continued fraction form of the Green function,

$$G_{\phi,\phi}(z) = \frac{1}{z - \alpha_1 + \frac{-\beta_1}{z - \alpha_2 + \frac{-\beta_2}{z - \alpha_3 + \cdots}}}, \quad (5.7)$$

where $\alpha$ and $\beta$ are tridiagonal elements when we tridiagonalize $H$ with the Lanczos method using $|\phi\rangle$ as the initial vector.

In the actual calculations, we chose $\eta = 2 \times 10^{-5}$ and $n_{\text{dim}} = 120$ and evaluated the continued fractions using the first 100 Lanczos coefficients. We construct $\rho_{L/2}^{(\text{cf})}(\omega)$ using the resultant distribution functions for the $S = 1/2$ systems and calculate the specific heat as

$$C = \beta^2 \left[ Z^{-1} \int d\omega \omega^2 \rho_{L/2}^{(\text{cf})}(\omega)e^{-\beta \omega} - E^2 \right], \quad (5.8)$$

where $\beta = \Gamma/T$, $Z = \int d\omega \rho_{L/2}^{(\text{cf})}(\omega)e^{-\beta \omega}$ and $E = Z^{-1} \int d\omega \omega \rho_{L/2}^{(\text{cf})}(\omega)e^{-\beta \omega}$. The calculated results are plotted in Fig. 12. In order to check the validity of our calculations, the exact specific heat for $L = 16$ is also shown. We find that the agreement between the result obtained with the finite-temperature Lanczos method for $L = 16$ (denoted
Fig. 12. Temperature dependence of the specific heat for $\Gamma/J = +0$ and $\lambda = 1$ calculated using the finite temperature Lanczos method, together with extrapolation to the thermodynamic limit, and the exact result for $L = 16$.

by the cross) and the exact one (denoted by the solid line) is satisfactory. With regard to the number of sampling vectors, $n_{\text{dim}}$, required for larger systems, it is reported in Ref. 14) that this number can be reduced while still realizing the same level of accuracy in the estimate of physical quantities, because of the self-averaging property. For this reason, we expect the accuracy of the calculations for $L = 24$, 28, 32 to be at least as good as that for $L = 16$. We use the data for the two largest systems in order to extrapolate to the thermodynamic limit, $L = \infty$, assuming $C/L \approx a + b/L^2$, following Ref. 14). In this way, we obtain our estimation of the specific heat for $L = \infty$ plotted by the thick gray line in Fig. 12. We find that the two-peak structure clearly exists even in the thermodynamic limit. Therefore, we conclude that the release of the residual entropy of an $S = 1$ Ising antiferromagnet on a $\Delta$ chain caused by small transverse crystal fields leads to a unique two-peak structure in the specific heat.

§6. Summary and discussion

In this paper, we have studied an $S = 1$ transverse crystal field Ising antiferromagnet on a $\Delta$ chain. Although Oittma and Brasch’s theorem ensures that the ground state property is essentially the same as that of an $S = 1/2$ transverse magnetic field Ising antiferromagnet, the existence of $S^z = 0$ states in this model, together with the frustrated nature of the lattice, leads to a unique three-staged entropy release for $\Gamma \ll J$.

We have pointed out that the introduction of the generalized model $H_\lambda$ is useful for understanding thermodynamic properties. The overall behavior of the specific heat changes continuously as $\lambda$ decreases. The model $H_{\lambda = 0}$ exhibits ground state degeneracy: Each tip spin can be in the $S^z = 0$ state or the $|S^z = 1\rangle + |S^z = -1\rangle$ state
in the ground state manifold. Therefore, we can consider the lowest temperature peak as the entropy release corresponding to the degrees of freedom of the tip spins.

In order to study the size dependence of the specific heat of $H (= H_{\lambda=1})$, we have developed a continuous time cluster algorithm for $S = 1$ transverse crystal field Ising models. By incorporating the exchange process into the algorithm, we have calculated the specific heat for systems with $L \leq 32$ and $\Gamma/J = 0.4$. We observed that the second lowest temperature peak tends to a shoulder as the system size is enlarged for the case $\Gamma/J = 0.4$.

We have also studied the size dependence of the specific heat at $\Gamma/J = +0$ using the finite temperature Lanczos method. We have carried out calculations up to $L = 32$, concentrating on the subspace with the minimum exchange energy and utilizing the conservation of $S^z = 0$ sites. We carried out an extrapolation to $L \rightarrow \infty$ and confirmed that the two peaks at $T \sim 0.05\Gamma$ and $0.2\Gamma$ remain in the thermodynamic limit.

The origin of the unique behavior of the model results from the fact that when only the tip spins are subject to a crystal field, the ground state degeneracy of the $S = 1$ $\Delta$ chain Ising model is not completely removed. Thus, we expect the generalized model $H_\lambda$ to exhibit the three-peak structure of the specific heat for $J \gg \Gamma$ and $\lambda \ll 1$, because three energy scales with considerably different magnitudes are contained in the model itself. However, it is surprising that the three-peak structure survives at $\lambda = 1$, where the model Hamiltonian contains only two energy scales, $J$ and $\Gamma$. In addition, there exists a quantum phase transition point, $\lambda_c(\Gamma/J = +0) = 0.946$, between $\lambda = 0$ and $\lambda = 1$. Although the reason for the existence of the additional energy scale at $\lambda = 1$ is not yet well understood, one important factor is thought to be the nonequivalence of the tip and bottom sites. It would also be interesting to study how the additional energy scale affects other thermodynamic quantities.

In conclusion, we have found that the simple spin-1 frustrated system described by $H$ exhibits an interesting thermodynamic property — three-staged entropy release — due to the existence of $S^z = 0$ states, even though the $S^z = 0$ states play no role in the ground state.

References