Reentrant phenomenon and inverse magnetocaloric effect in a generalized spin-(1/2, s) Fisher’s super-exchange antiferromagnet

Lucia Gálisová

Department of Applied Mathematics and Informatics, Faculty of Mechanical Engineering, Technical University of Košice, Letná 9, 042 00 Košice, Slovakia

E-mail: galisova.lucia@gmail.com

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Abstract
The thermodynamic and magnetocaloric properties of a generalized spin-(1/2, s) Fisher’s super-exchange antiferromagnet are investigated precisely by using the decoration-iteration mapping transformation. Besides the critical temperature, sublattice magnetization, total magnetization, entropy and specific heat, the isothermal entropy change and adiabatic temperature change are also rigorously calculated in order to examine the cooling efficiency of the model in the vicinity of the first- and second-order phase transitions. It is shown that an enhanced inverse magnetocaloric effect occurs around the temperature interval \( T_d(B = 0) \lesssim T < T_c(B = 0) \) for any magnetic-field change \( \Delta B : 0 \rightarrow B \). The most pronounced inverse magnetocaloric effect can be found nearby the critical field, which corresponds to the zero-temperature phase transition from the long-range ordered ground state to the paramagnetic one. The observed phenomenon increases with an increasing value of decorating spins. Furthermore, sufficiently high values of decorating spins have also been linked to the possibility of observing reentrant phase transitions at finite temperatures.

Keywords: Fisher’s super-exchange antiferromagnet, reentrant phenomenon, thermodynamics, magnetocaloric effect

(Some figures may appear in colour only in the online journal)
latter one can be detected in ferrimagnetic and antiferromagnetic materials. Moreover, the coexistence of both phenomena is also possible. In fact, conventional and inverse MCEs have been theoretically observed in magnetic systems with a rich ground-state phase diagram structure, in particular, in various one-dimensional spin models [5, 6, 9–24], some finite structures [7, 8, 25–27] and multilayers [28]. However, the enhanced MCE has so far only been rigorously investigated in one-dimensional systems [5, 6, 9–24] or in some finite structures [25, 27] due to a lack of precisely solved spin models in higher dimensions accounting for a non-zero magnetic field. A theoretical description of this phenomenon in two- and three-dimensional magnetic systems is usually only based on some approximative methods [28–32].

In 1960, Fisher proposed a novel spin-1/2 super-exchange Ising antiferromagnet on a decorated square lattice to permit a rigorous solution of the partition function in the presence of an external magnetic field [33, 34]. The spin-1/2 Fisher’s super-exchange model and its other variants [35–38] can thus be used for an exact theoretical study of the effect of applied fields on the magnetic properties of a certain class of magnetic insulators, e.g. for the investigation of the cooling or heating efficiency of the system in the vicinity of discontinuous (first-order) and continuous (second-order) phase transitions. In addition, these spin models may also produce considerable insight into the deficiencies of some approximative methods. Motivated by the aforementioned facts, the purpose of this paper is to extend the rigorous theoretical examination of the MCE to a class of two-dimensional spin models. We will consider the generalized spin-(1/2, s) Fisher’s super-exchange model on a decorated square lattice in order to gain a deeper insight into how the critical behavior of the model depends on the magnitude of the decorating spins. Particular attention will be paid to the examination of regions showing an enhanced MCE.

The outline of the paper is as follows: in section 2, a generalization of the Fisher’s super-exchange model together with a brief description of its exact analytical treatment will be carried out. In section 3, the most interesting results for the ground state, the finite-temperature phase diagram as well as the magnetization, specific heat and entropy will be discussed. The magnetocaloric properties of the model will be presented in detail in section 4. Finally, section 5 will regard the conclusions and future outlook.

2. Model and its exact solution

Let us consider a mixed spin-(1/2, s) Ising model on a decorated square lattice involving the effect of an external magnetic field, as is schematically depicted in figure 1. In this figure, the empty circles denote the nodal lattice sites occupied by the Ising spins $\sigma = 1/2$, while the full ones label the decorating lattice sites occupied by the Ising spins of an arbitrary magnitude $s$. Because the two-dimensional Ising model, all of whose spins are placed into the external magnetic field, still represents an unsolvable problem of statistical mechanics, we will further assume the simplified version of the model, in which the longitudinal magnetic field $B$ just acts on the decorating spins. In addition, exchange interactions of the same intensity but of opposite signs have to be supposed between the nearest spin neighbors in the horizontal and vertical directions to ensure the exact tractability of the considered spin system. For this reason, we will further assume the ferromagnetic (antiferromagnetic) coupling $-J < 0$ ($J > 0$) on the horizontal (vertical) bonds of the lattice. Under the above assumptions, the total Hamiltonian of the model reads

$$\mathcal{H} = -J\sum_{i,\ell}^N \sigma_i \sigma_\ell + J\sum_{\langle i,\ell \rangle}^N \sigma_i \sigma_\ell - B\sum_{k=1}^N \sigma_k - B\sum_{l=1}^N \sigma_l,$$

(1)

where $\sigma_\ell = -s, -s + 1, \ldots, s$ labels the decorating Ising spin at the $\ell$th horizontal ($\ell$th vertical) bond and $\sigma_i = \pm 1/2$ denotes the nodal Ising spin at the $i$th site of the original square lattice. The first (second) summation in the Hamiltonian (1) is carried out over nearest-neighboring lattice sites in the horizontal (vertical) direction, while two terms represent the Zeeman energies of the decorating spins. Finally, $N$ represents the total number of nodal sites of the original lattice, i.e. the Ising spins $\sigma$ (we consider the thermodynamic limit $N \to \infty$). It is worth emphasizing that the considered spin model is generally slightly different from the usual antiferromagnetic Ising square lattice. In particular, the standard antiferromagnetic model becomes ferromagnetic when the sign of the exchange integral $J$ is changed. By contrast, the Hamiltonian (1) remains invariant against the transformation $J \rightarrow -J$.

The two-dimensional spin model defined in the above way is exactly solvable within the framework of a generalized decoration-iteration mapping transformation [39–41]. More specifically, the different signs of the exchange constants on the horizontal and vertical bonds of the decorated square lattice cancel out the contributions of the mapping terms that represent effective magnetic fields acting on nodal spins of the corresponding simple lattice (for more computational details see Fisher’s original works [33, 34] and our previous work [38]). As a result, one obtains a simple relation between the partition function $Z_\Phi$ of the considered mixed spin-(1/2, s) Fisher’s super-exchange model (1) and the partition function

Figure 1. The spin-(1/2, s) Fisher’s super-exchange model on a decorated square lattice. The empty circles denote nodal lattice sites occupied by the Ising spins $\sigma = 1/2$, while the full circles mark the lattice positions of the decorating Ising spins of arbitrary magnitude $s$.
\( Z_1 \) of the spin-1/2 Ising model on a simple square lattice defined by the Hamiltonian \( H_1 = -J_{\text{eff}} \sum_{<i,j>} \sigma_i \sigma_j \):

\[
Z_{\beta}(J, B, s) = \Lambda^N Z_{1}(\beta, J, \text{eff})).
\]  

(2)

Above, \( \beta = 1/(k_B T) \) is the inverse temperature (\( k_B \) is Boltzmann’s constant) and the mapping parameters \( A \) and \( J_{\text{eff}} \) are unambiguously determined by a ‘self-consistency’ condition of the applied decoration-iteration transformation.

At this stage, the exact treatment of the generalized Fisher’s super-exchange model is formally completed, because the partition function \( Z_{\beta} \) of the spin-1/2 Ising model on the square lattice is well known [42]:

\[
\ln Z_{1} = N \ln 2 + \frac{N}{2 \pi^2} \int_{0}^{\pi} \int_{0}^{\pi} \ln(C^2 - S \cos \theta - S \cos \phi) d\theta d\phi.
\]  

(3)

Here, \( C = \cosh(\beta J_{\text{eff}}/2) \) and \( S = \sinh(\beta J_{\text{eff}}/2) \). Actually, equation (2) in combination with the exact mapping theorems developed by Barry et al [43–46] and the generalized Callen–Suzuki spin identity [47–49] allow us to rigorously express the spontaneous magnetization \( m_{s} \) of the nodal spins, as well as the magnetizations \( m_h \) and \( m_v \) of the decorating spins located on the horizontal and vertical bonds, respectively:

\[
m_{s} \equiv \langle \sigma_i \rangle = \langle \sigma_i \rangle_1 \equiv m_{t}, \tag{4}
\]

\[
m_{h} \equiv \langle \sigma_i \rangle = K - 4m_{L} + 4c_{1}M, \tag{5}
\]

\[
m_{v} \equiv \langle \sigma_i \rangle = K + 4m_{L} + 4c_{1}M. \tag{6}
\]

Above, the symbols \( \langle \cdots \rangle \) and \( \langle \cdots \rangle_1 \) denote the standard canonical ensemble average performed over the generalized spin-(1/2, s) Fisher’s model (1) and the corresponding spin-1/2 Ising model on a square lattice, respectively. Obviously, the aforelisted magnetization is expressed in terms of the spontaneous magnetization \( m_{t} \) and the two-spin correlation function \( c_1 \) between the nearest-neighboring spins of the spin-1/2 Ising square lattice. Since rigorous solutions for both quantities are well known [50, 51], we can restrict ourselves just to the appointment of the coefficients \( K, L \) and \( M \):

\[
K = F(J) + F(-J) + 2F(0), \\
L = F(J) - F(-J), \\
M = F(J) + F(-J) - 2F(0),
\]  

(7)

where the function \( F(x) \) is defined as

\[
F(x) = \frac{1}{4} \sum_{n=-x}^{n=x} \frac{1}{n} \sinh[n(x - B)].
\]  

(8)

In view of this notation, the total magnetization \( m_{s}^{*} \) and the staggered magnetization \( m_{n}^{*} \) of the decorating spins normalized per one nodal site of the decorated lattice can be expressed as

\[
m_{s}^{*} = \frac{1}{2}(m_{h} + m_{v}) = K + 4c_{1}M, \tag{9}
\]

\[
m_{n}^{*} = \frac{1}{2}(m_{h} - m_{v}) = -4m_{L}. \tag{10}
\]

The other important thermodynamic quantities, such as the Gibbs free energy \( G \), the entropy \( S \) and the specific heat \( C \) can easily be obtained from the relations:

\[
G = -k_B T \ln Z_{1} - 2Nk_B T \ln A, \tag{11}
\]

\[
S = -\left( \frac{\partial G}{\partial T} \right)_B, \quad C = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_B. \tag{12}
\]

Finally, let us make a few comments on the critical behavior of the model. It is clear from the mapping relation (2) that the generalized Fisher’s super-exchange model on the decorated square lattice may exhibit a critical point, only if the corresponding spin-1/2 Ising model on the undecorated square lattice is at a critical point as well. As a consequence, the critical temperature of the mixed spin-(1/2, s) Fisher’s super-exchange model can be straightforwardly obtained by comparing the effective nearest-neighbor coupling of the corresponding spin-1/2 Ising model on the simple square lattice with its critical value [42]:

\[
\beta J_{\text{eff}} = 2 \ln(1 + \sqrt{2}), \tag{13}
\]

where \( \beta_s = 1/(k_B T_c) \) and \( T_c \) denotes the critical temperature of the studied spin model.

3. Ground-state and finite-temperature properties

In this section, we present the most interesting numerical results for the ground state, the finite-temperature phase diagram as well as thermal dependencies of the magnetization, entropy and specific heat of the mixed spin-(1/2, s) Fisher’s super-exchange model on the decorated square lattice.

First, let us start with a brief description of the ground-state behavior\footnote{Because we consider the generalization of the original Fisher’s super-exchange model in terms of the magnitude \( s \) of decorating spins, the presented analysis also includes the particular spin case \( s = 1/2 \), which was discussed by Fisher several decades ago [33, 34].}. At zero temperature, the investigated spin model passes from the long-range ordered ground state to the paramagnetic one when the magnetic field applied to the decorating spins exceeds the critical value \( B_c/J = 1 \). The former ground state is characterized by a perfect antiferromagnetic arrangement of decorating spins placed on the horizontal and vertical bonds of the lattice (\( m_h = s, m_v = -s \)) and by the saturated spontaneous magnetization \( m_s = 1/2 \) attributed to nodal spins. In the latter ground state, all decorating spins are fully polarized towards the magnetic-field direction, while the nodal spins are frustrated due to the mutual competition between the ferromagnetic and antiferromagnetic exchange interactions (\( m_h = m_v = s, m_n = 0 \)).
As expected, at finite temperatures, the long-range antiferromagnetic order of the decorating spins completely vanishes at the critical temperature given by equation (13). For a better illustration, the critical temperature versus magnetic field is displayed in figure 2 for three different values of decorating spins. Note that the plotted curves are unique solutions of the critical condition (13) and therefore, they present the lines of continuous (second-order) phase transitions between the long-range ordered and paramagnetic phases. As one can see from figure 2, the critical temperature of the model generally decreases with the increasing magnetic field until it entirely tends to zero at the critical field $B_c/J = 1$ of the first-order phase transition between the long-range ordered and paramagnetic ground states. For the decorating spins $s < 5/2$, critical lines approach the first-order phase transition with negative slopes, while for the reverse case $s > 5/2$, they approach the critical field $B_c/J = 1$ with positive slopes. These observations clearly suggest that reentrant phase transitions appear in the magnetic-field region $BJ \gtrsim 1$ just for sufficiently high decorating spins $s \gtrsim 5/2$. As can be expected, the observed reentrant phenomenon becomes more pronounced the higher the spin value $s$ is.

To confirm the above findings, the temperature dependencies of the spontaneous magnetization $m_c$ of the nodal spins (broken lines) and the staggered magnetization $m_s$ of the decorating spins are plotted in figure 3 for two particular spin values $s = 1$ and $s = 4$ by assuming different values of the external magnetic field applied to those spins. For easy reference, we will further use the extended Néel’s classification of $m(T)$ curves [52–54]. As one can see from figure 3, both magnetizations start from their saturated values $m_c = 1/2$ and $m_s = s$ if the applied magnetic field is lower than the critical value $B_c/J = 1$. Moreover, the spontaneous magnetization of the nodal spins exhibits solely familiar Q-type dependencies characterized by a steep decrease in magnetization just in the vicinity of the critical temperature (see the $m_c(T)$ curves plotted for $B/J = 0.6$, 0.9, 0.98 in figures 3(a) and (b)). By contrast, the temperature dependencies of the staggered magnetization of the decorating spins may change from conventional R-type curves to more interesting S-type curves if the values of the decorating spins are high enough and the external magnetic field takes the values $B \lesssim B_c$ (see the $m_s(T)$ curves corresponding to $B/J = 0.6$, 0.9 and 0.98 in figure 3(b)). The R-type dependencies exhibit a relatively rapid decline in magnetization within the range of intermediate temperatures before a sharp drop to zero magnetization at the critical point. The S-type dependencies show two sharp magnetization decreases; the first one, which can be observed at low temperatures, almost completely diminishes in the range of intermediate temperatures, and the second one is located near the critical temperature. The origin of all three types of magnetization curves closely relates to the fact that the longitudinal magnetic field $B$ does not directly act on nodal spins, but only on decorating spins localized at horizontal and vertical bonds of the lattice. Hence, the spontaneous magnetization $m_c$ varies very smoothly with temperature, while the staggered magnetization $m_s$ declines more rapidly as the temperature increases before reaching the critical point. As expected, the observed temperature decrease of $m_c$ is more rapid the closer to the critical field $B_c/J = 1$ we are. For the particular case $B_c/J = 1$, the magnetizations $m_c$ and $m_s$ acquire zero-temperature asymptotic values unambiguously given by the general conditions

$$m_c(T = 0) = \begin{cases} 0 & \text{for } s < 5/2, \\ \frac{1}{2} \left(1 - \frac{2s + 1}{s^2}\right)^{1/8} & \text{for } s \gtrsim 5/2, \end{cases} \quad (14)$$

as illustrated in figure 3. The above analytical expressions for $m_c$ and $m_s$ indicate that the investigated spin-(1/2, 2) Fisher’s super-exchange model exhibits an interesting macroscopic degeneracy at $B_c/J = 1$, which originates from the mutual interplay between the magnetic field applied to the decorating spins and the ferromagnetic as well as antiferromagnetic exchange interactions between the nearest-neighboring spins in the horizontal and vertical directions, respectively. Finally, by considering sufficiently high values of decorating spins $s \gtrsim 5/2$, one can observe the reentrant behavior in thermal variations of both the magnetizations $m_c$ and $m_s$ with two consecutive critical points for the magnetic fields $BJ > 1$ (see the curves plotted for $B/J = 1.02$ in figure 3(b), which unambiguously confirms the former analysis of the critical behavior of the studied model.

In order to complete the analysis of the magnetization, let us turn our attention to the temperature dependencies of the magnetizations $m_c^+$, $m_h$ and $m$ that are illustrated in figure 4. The following general conclusions can be deduced from the plotted $m_s^+(T)$ curves. Depending on the intensity of the applied magnetic field, the total magnetization $m_s^+$ can asymptotically reach three different values as the temperature tends to zero, namely,

$$m_s^+(T = 0) = \begin{cases} 0 & \text{for } B < B_c, \\ \frac{2s + 1}{4} + \frac{2s + 1}{\pi(s + 1)} \left(\frac{s\sqrt{2s + 1}}{s + 1}\right) & \text{for } B = B_c, \\ \frac{s}{s + 1} & \text{for } B > B_c, \end{cases} \quad (16)$$
where $\mathcal{K}(x) = \int_0^{\pi/2} (1 - x^2 \sin^2 \phi)^{-1/2} d\phi$ is a complete elliptic integral of the first kind. In the low-temperature region, $m_\sigma^+$ shows a noticeable increase (decrease) with increasing temperature if the magnetic field takes lower (higher) values than $B_c/J = 1$. As expected, these temperature-induced changes of $m_\sigma^+$ are more pronounced the closer the magnetic field is to the critical value $B_c/J = 1$. The rapid variations of $m_\sigma^+$ observed in the temperature regime $T < T_c(B = 0)$ are evidently associated with the predominant temperature-induced excitations of the decorating spins located at vertical bonds of the lattice, which are also clearly reflected in an unusually steep low-temperature variation of the corresponding magnetization $m_\sigma$, (see the insets in figures 4(a) and (b)). Moreover, one or two weak energy-type singularities can also be found in the $m_\sigma^+(T)$ curves at critical temperatures relevant to the continuous phase transitions between the long-range ordered state and the paramagnetic state dependent on the magnitude of the decorating spins and the intensity of the magnetic field applied to them. One can also see from figure 4, where these singularities are denoted by full circles, that the magnetization $m_\sigma^+$ exhibits an interesting broad local maximum above the critical temperature, at which the studied spin system passes from the long-range ordered state to the paramagnetic state as the temperature increases. As demonstrated by Fisher [33], the intriguing temperature-induced increase of $m_\sigma^+$ indicates the presence of residual short-range ordering in the the temperature region $T > T_c(B = 0)$. On the other hand, if decorating spins are high enough to form reentrant critical behavior in the field region $B_c/J < 1$, then a sharp drop in the temperature dependencies of $m_\sigma^+$ resulting in a local minimum can be detected in the relatively narrow temperature range between two successive singularities (see the curve plotted in figure 4(b) for the magnetic field $B/J = 1.02$).
Now, let us look in detail at the temperature variations of basic thermodynamic quantities such as the entropy and specific heat. Figure 5 shows the temperature dependencies of the entropy normalized per one nodal site of the decorated square lattice calculated for one representative spin value $s = 4$ and a few different values of the magnetic field $B$ (main figure) as well as for three different values of decorating spins by assuming the critical field $B_c/J = 1$.

![Figure 5](image)

Figure 5. Temperature variations of the entropy for the spin case $s = 4$ and several fixed values of the magnetic field $B$. Inset: low-temperature variations of the entropy for three selected values of decorating spins assuming the critical field $B_c/J = 1$.

Recall that the former relation (17) is valid if the temperature of the model is constant, while the latter relation (18) satisfies the adiabatic condition $S = \text{const}$.

Figure 7 shows the temperature dependencies of the iso-thermal entropy change normalized per site of the original square lattice ($-\Delta S_T/Nk_B$) for two particular values of decorating spins $s = 1$ and $s = 4$ by considering various magnetic-field changes $\Delta B : 0 \rightarrow B$. As one can see, the iso-thermal entropy change may either be positive or negative depending on the temperature, which clearly points to both a conventional ($-\Delta S_T > 0$) and an inverse ($-\Delta S_T < 0$) MCE for any magnetic-field change $\Delta B$. Namely, in the high-temperature region $T \gg T_c(B = 0)$, where only short-range ordering occurs, $-\Delta S_T$ is always positive and slowly increases to the broad maximum with decreasing temperature due to suppression of the spin disorder by the applied magnetic field. At a certain temperature, $-\Delta S_T$ starts to rapidly decrease and changes sign from positive to negative as the temperature further decreases.

Since the investigated spin-(1/2, s) Fisher’s super-exchange model on a decorated square lattice (1) is exactly solvable within the generalized decoration-iteration mapping transformation [39–41], it provides an excellent paradigmatic example of a precisely soluble two-dimensional spin system, which allows an examination of the MCE in the vicinity of the continuous phase transition in the finite magnetic fields. Actually, the magnetocaloric quantities, such as the isothermal entropy change $\Delta S_T$ and the adiabatic temperature change $\Delta T_{\text{ad}}$ upon the magnetic-field variation $\Delta B : 0 \rightarrow B$ can be rigorously calculated by using the following formulas:

$$\Delta S_T(T, \Delta B) = S(T, B = 0) - S(T, B = 0),$$

$$\Delta T_{\text{ad}}(S, \Delta B) = T(S, B = 0) - T(S, B = 0).$$

Recall that the former relation (17) is valid if the temperature of the model is constant, while the latter relation (18) satisfies the adiabatic condition $S = \text{const}$.

The origin of this value cannot be explained by a simple argument. It is possible just to say that it is determined by the cooperative action of the whole lattice.

Finally, we conclude the analysis of thermodynamics with a description of the typical temperature dependencies of the specific heat that are displayed in figure 6. To enable a direct comparison, we have chosen the values of the external magnetic field and decorating spins so as to match the finite-temperature phase diagram shown in figure 2 and also the temperature dependencies of the magnetization plotted in figures 3 and 4. In this manner, the depicted specific heat curves reflect a comprehensive picture of the finite-temperature behavior of the investigated spin system. In fact, besides the one or two logarithmic divergences at the appropriate critical temperatures, marked local maxima can be detected in the low-temperature tails of the specific heat curves if the external magnetic field takes the values from a close vicinity of the first-order phase transition between the long-range ordered ground state and the paramagnetic ground state. A direct comparison of the specific heat curves depicted in figure 6 for the magnetic fields $B/J = 0.9$ and 1.02 with the corresponding magnetizations $m^c_s$, $m^-_s$ and $m^+_s$ shown in figures 3 and 4 confirms that the origin of the observed low-temperature maxima lies in the strong thermal excitations to a spin configuration rather close in energy to the ground state.

4. Magnetocaloric properties

Since the investigated spin-(1/2, s) Fisher’s super-exchange model on a decorated square lattice (1) is exactly solvable within the generalized decoration-iteration mapping transformation [39–41], it provides an excellent paradigmatic example of a precisely soluble two-dimensional spin system, which allows an examination of the MCE in the vicinity of the continuous phase transition in the finite magnetic fields. Actually, the magnetocaloric quantities, such as the isothermal entropy change $\Delta S_T$ and the adiabatic temperature change $\Delta T_{\text{ad}}$ upon the magnetic-field variation $\Delta B : 0 \rightarrow B$ can be rigorously calculated by using the following formulas:

$$\Delta S_T(T, \Delta B) = S(T, B = 0) - S(T, B = 0),$$

$$\Delta T_{\text{ad}}(S, \Delta B) = T(S, B = 0) - T(S, B = 0).$$

Recall that the former relation (17) is valid if the temperature $T$ of the model is constant, while the latter relation (18) satisfies the adiabatic condition $S = \text{const}$. 

Figure 7 shows the temperature dependencies of the iso-thermal entropy change normalized per site of the original square lattice ($-\Delta S_T/Nk_B$) for two particular values of decorating spins $s = 1$ and $s = 4$ by considering various magnetic-field changes $\Delta B : 0 \rightarrow B$. As one can see, the iso-thermal entropy change may either be positive or negative depending on the temperature, which clearly points to both a conventional ($-\Delta S_T > 0$) and an inverse ($-\Delta S_T < 0$) MCE for any magnetic-field change $\Delta B$. Namely, in the high-temperature region $T \gg T_c(B = 0)$, where only short-range ordering occurs, $-\Delta S_T$ is always positive and slowly increases to the broad maximum with decreasing temperature due to suppression of the spin disorder by the applied magnetic field. At a certain temperature, $-\Delta S_T$ starts to rapidly decrease and changes sign from positive to negative as the temperature further decreases.
inverse MCE can be attributed to strong thermal fluctuations of spins leading to an unusual increase of the total magnetization $m_s^+$ in this region (compare the $-\Delta S_T(T)$ curves plotted in the upper panel in figure 7(a) with the corresponding temperature variations of the magnetization $m_s^+$ shown in figure 4(a)). A more complex scenario occurs if the decorating spins take higher values than $s = 1$. Two local minima can be observed in the low-temperature parts of the $-\Delta S_T(T)$ curves for

Figure 6. Temperature variations of the specific heat for the same decorating spins as in figures 3 and 4 by considering a few fixed values of the magnetic field $B$.

Figure 7. Temperature variations of the isothermal entropy change normalized per one nodal lattice site ($-\Delta S_T/Nk_B$) for the same decorating spins as in figures 3–6 by considering few magnetic-field changes $\Delta B : 0 \rightarrow B$. Empty and full circles mark weak singularities of the entropy located at critical points of the continuous phase transitions at zero and the respective non-zero magnetic fields, respectively.
provided the decorating spins are high enough. Indeed, one minimum can be detected in the temperature range \( T < T_c(B = 0) \) with an increasing intensity of applied magnetic field, as shown in the upper panel in figure 7(b) for the representative spin case \( s = 4 \). Obviously, if the magnetic-field change approaches \( B/J : 0 \rightarrow 1 \), these two local minima gradually merge into one pronounced minimum located far below the critical temperature \( T_c(B = 0) \) (see the curve corresponding to \( B/J : 0 \rightarrow 0.98 \) in the upper panel of figure 7(b)). It is justified to suppose that the enhanced inverse MCE detected below \( T_c(B = 0) \) comes from strong thermal excitations of the decorating spins placed on vertical bonds of the lattice, which are reflected in a sharp temperature-induced increase of the corresponding magnetization \( m_v \) and, subsequently, also the magnetization \( m_s \) (compare the \( -\Delta S_f(T) \) curve plotted in the upper panel of figure 7(b) for \( B/J : 0 \rightarrow 0.98 \) with the corresponding temperature dependencies of the magnetizations \( m_v \) and \( m_s \) displayed in figure 4(b)). As expected, this inverse MCE enlarges with the increasing spin value \( s \) due to the increase of predominant thermal excitations of decorating spins placed on the vertical bonds of the lattice (not shown). Furthermore, it is quite obvious from figure 7 that

\[ -\Delta S_f(T, B : 0 \rightarrow 1) < -\Delta S_f(T, B : 0 \rightarrow B = 1) \]

is satisfied if the temperature approaches the zero value. Thus, one may conclude that the most pronounced inverse MCE can always be found for the magnetic-field change \( B/J : 0 \rightarrow 1 \), which exactly coincides with the critical field \( B_{Jc} = 1 \) of the first-order phase transition between the magnetically ordered and paramagnetic ground states. Finally, for \( B/J > 1 \), the inverse MCE (minimum in \( -\Delta S_f(T) \) curves) is gradually reduced with increasing \( B \) due to the weakening of thermal excitations from the paramagnetic ground state towards the long-range ordered excited state (see lower panels in figure 7).

To discuss the MCE, one may alternatively examine the adiabatic temperature change \( \Delta T_{ad} \) of the system at various magnetic-field changes \( B : 0 \rightarrow B \). The typical temperature variations of this magnetocaloric potential for the considered model are displayed in figure 8. Note that all curves plotted in figure 8 were calculated using equation (18) by keeping the entropy constant. As one can see, the adiabatic temperature change \( \Delta T_{ad} \) clearly allows us to distinguish the conventional MCE (\( \Delta T_{ad} > 0 \)) from the inverse MCE (\( \Delta T_{ad} < 0 \)). In accordance with the previous discussion, the investigated spin system generally heats up as fast as possible in close vicinity of the first-order phase boundary between the long-range ordered and paramagnetic ground states achieved upon

\[ \Delta B/J \in (0, 1) \]
an adiabatic reduction of the magnetic field, regardless of the magnitude of the decorating spins. Indeed, the magnitude of the negative peak in the $\Delta T_{ad}(T)$ curves gradually increases with the magnetic-field change $\Delta B$ (see the upper panels of figure 8). In addition, $\Delta T_{ad}$ versus the temperature plots end at a zero value in the asymptotic limit of zero temperature for any $\Delta B/J \in (0, 1)$, which can be attributed to the perfect antiferromagnetic order of decorating spins placed on the horizontal and vertical bonds of the square lattice at zero temperature. By contrast, the adiabatic temperature change rapidly drops to finite negative values at certain temperatures when the applied magnetic field is equal to or higher than the critical value $B_c/J = 1$ (see lower panels in figure 8). In this particular case, the magnetocaloric potential $\Delta T_{ad}$ cannot be defined below the aforementioned temperatures, because there is no temperature end point in the adiabatic process if $B/J \geq 1$. This intriguing behavior is evidently caused by the residual entropies found at the coexistence point $B_c/J = 1$ of the first-order phase transition and within the paramagnetic ground state (see figure 5).

5. Summary and future outlook

The present work deals with the thermodynamics and magnetocaloric properties of the generalized spin-(1/2, $\sigma$) Fisher’s super-exchange antiferromagnet on the decorated square lattice. Exact results for the critical temperature, total and sublattice magnetization, specific heat and entropy have been derived and discussed in detail for a few representative values of decorating spins. It has been shown that the studied mixed-spin model exhibits reentrant phase transitions with two consecutive critical points slightly above the critical field $B_c/J = 1$ corresponding to the first-order phase transition between the long-range ordered and paramagnetic ground states, if the decorating spins take the sufficiently high values $s \geq 5/2$. The existence of this non-trivial phenomenon has also been confirmed by the temperature variations of the spontaneous and staggered magnetization of the nodal and decorating spins, respectively, as well as by the remarkable temperature dependencies of the specific heat exhibiting two logarithmic singularities.

Moreover, the MCE has been particularly examined by means of the isothermal entropy change and the adiabatic temperature change. The investigation of both magnetocaloric potentials has enabled us to rigorously clarify the magnetic refrigeration efficiency of the considered spin model in the vicinity of the first-order phase transition between the long-range ordered ground state and the paramagnetic ground state as well as near the critical temperature, which completely destroys the antiferromagnetic long-range order. The obtained results clearly indicate the fast heating of the studied mixed-spin system during the adiabatic demagnetization process (i.e. the presence of an enhanced inverse MCE) in these regions due to strong thermal spin fluctuations leading to a temperature-induced increase of the total magnetization corresponding to the decorating spins. The maximal heating efficiency of the system has been observed for the magnetic-field change $\Delta B/J : 0 \to 1$, which coincides with the first-order phase transition between the long-range ordered and paramagnetic ground states.

Finally, it is worth mentioning that the presented generalization of the Fisher’s super-exchange antiferromagnet on a decorated lattice in terms of arbitrary decorating spins is just one of many possibilities. Other simple generalizations allowing the rigorous investigation of an enhanced MCE in two-dimensional spin systems are the introduction of the second-neighbor interaction between nodal spins [35], the introduction of the chemical potential [36], the axial zero-field splitting [38], the transverse magnetic field as well as the rhombo zero-field splitting on decorating spins. Moreover, one may also consider other planar lattices with even coordination numbers, such as the Kagomé lattice and the triangular lattice. Our future work will continue in this direction.

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