Magnetic Grüneisen parameter and magnetocaloric properties of a coupled spin-electron double-tetrahedral chain

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Abstract
Magnetocaloric effect in a double-tetrahedral chain, in which nodal lattice sites occupied by the localized Ising spins regularly alternate with three equivalent lattice sites available for mobile electrons, is exactly investigated by considering the one-third electron filling and the ferromagnetic Ising exchange interaction between the mobile electrons and their nearest Ising neighbours. The entropy and the magnetic Grüneisen parameter, which closely relate to the magnetocaloric effect, are exactly calculated in order to investigate the relation between the ground-state degeneracy and the cooling efficiency of the hybrid spin-electron system during the adiabatic demagnetization.

Keywords: spin-electron double-tetrahedral chain, magnetocaloric effect, entropy, magnetic Grüneisen parameter, exact results

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1. Introduction
The magnetocaloric effect (MCE), which is characterized by an adiabatic change of the temperature (or by an isothermal change of the entropy) under the variation of the applied magnetic field, has a long history in cooling applications at various temperature regimes [1]. Since the first successful experiment of the adiabatic demagnetization performed in 1933 [2], the MCE is a standard technique for achieving the extremely low temperatures [3].

The theoretical prediction and description of materials with an enhanced or even giant MCE create real opportunities for the effective selection of the construction for working magnetic refrigeration devices. Of particular interest is the investigation of the MCE in various one-dimensional (1D) quantum spin systems [4–13] or hybrid spin-electron models [14–16]. The reason is a possibility of obtaining the exact analytical or numerical results as well as a potential use of these models for the explanation of MCE data measured for real magnetic compounds. In particular, 1D models may give correct quantitative description of real three-dimensional (3D) magnets, when appropriate rescaling of material parameters are taken into account [17–20].

In the present Letter, we will investigate the MCE in a hybrid double-tetrahedral chain composed of the localized Ising spins and mobile electrons, which is exactly solvable by combining the generalized decoration-iteration mapping transformation [21–24] and the transfer-matrix technique [25, 26]. As has been shown in our previous works [15, 16], the considered 1D spin-electron system provides a suitable prototype model for theoretical investigation of the relation between the ground-state degeneracy and the cooling efficiency of the system during the adiabatic (de)magnetization.

The Letter is organized as follows. In Section 2, we will describe the investigated spin-electron double-tetrahedral chain and then, the basic steps of an exact analytical treatment of the model will be briefly recalled. Exact calculations of the basic thermodynamic quantities, such as the Gibbs free energy, the total magnetization, the entropy and the magnetic Grüneisen parameter, will be realized in this section. In Section 3, we will particularly discuss the numerical results acquired for the ground state, the entropy and the magnetic Grüneisen parameter as functions of the applied magnetic field under the assumption of the one-third electron filling of each triangular cluster and the ferromagnetic exchange interaction between the mobile electrons and their nearest Ising neighbours. Finally, the Letter ends up with a summary of our findings in Section 4.

2. Model and its exact solution
Let us consider a magnetic system on a double-tetrahedral chain, where nodal lattice sites occupied by the localized Ising spins regularly alternate with three equivalent lattice sites available to two mobile electrons. The magnetic structure of the considered 1D spin-electron model is schematically illustrated in Fig. 1. Assuming the exchange interactions between the nearest neighbours, the on-site Coulomb repulsion $U \geq 0$ between two electrons of opposite spins occupying the same lattice site and the action of the external magnetic field $B$ on the mobile electrons and the localized Ising spins, the total Hamiltonian of

\[ H = -J \sum \langle \tau \rangle \cdot \hat{S} - U \sum \delta(\sigma, \sigma') \hat{n}_\sigma - B \sum \hat{S}_z, \]

where $J$ is the exchange constant, $U$ is the on-site Coulomb repulsion, $\delta(\sigma, \sigma')$ is the Kronecker delta function, $\hat{n}_\sigma$ is the operator of one electron occupation on the site with spin $\sigma$, and $\hat{S}_z$ is the operator of the total magnetization along the $z$-axis.
the model reads:

\[
\mathcal{H} = -t \sum_{\langle i,j \rangle} \left( c^\dagger_i c_{j,s} + c^\dagger_j c_{i,s} \right) + \frac{J}{2} \sum_{\langle j,k \rangle} \left( n_{j,\uparrow} - n_{j,\downarrow} \right) \sigma^z_k + U \sum_j n_{j,\uparrow} n_{j,\downarrow} - \beta H \sum_j \sum_k \sigma^z_k. \tag{1}
\]

In above, the summation \( \langle i,j \rangle \) runs over the lattice sites forming triangular clusters, while the summation \( \langle j,k \rangle \) runs over the lattice sites of triangular clusters and the nearest-neighbouring nodal lattice sites. The operator \( c^\dagger_i c_{j,s} \) (or \( c^\dagger_j c_{i,s} \)) represents usual fermionic creation (annihilation) operator for mobile electrons occupying the \( j \)th lattice site with the spin \( s \in \{\uparrow, \downarrow\} \). \( n_{j,s} = c^\dagger_j c_{j,s} \) is the number operator of the mobile electron at the \( j \)th lattice site and \( \sigma^z_k \) labels the localized Ising spin at the \( k \)th nodal lattice site. The hopping parameter \( t > 0 \) takes into account the kinetic energy of mobile electrons delocalized over triangular clusters and \( J \) stands for the Ising-type coupling between mobile electrons and their nearest Ising neighbours. Finally, the last two terms in Eq. (1) represent the Zeeman’s energies of the mobile electrons and the localized Ising spins, which may be in general different due to a difference in the relevant Landé g-factors absorbed into the definition of the ’effective’ magnetic fields \( H_r = g_r \mu_B B \) and \( H_I = g_I \mu_B B \) (\( g_r \) is Landé g-factor of the mobile electrons, \( g_I \) is Landé g-factor of the localized Ising spins and \( \mu_B \) is Bohr magneton).

2.1. Partition function

One can note that the spin-electron model under consideration can alternatively be viewed as the spin-1/2 Ising linear chain, whose bonds are decorated by triangular clusters available for two mobile electrons. From this point of view, the partition function of the system can exactly be derived within the generalized decoration-iteration mapping transformation \([21–24]\) (as described in our previous work \([16]\)). As a result, one obtains a simple relation between the partition function \( Z \) of the investigated spin-electron tetrahedral chain and the partition function \( Z_I \) of the uniform spin-1/2 Ising linear chain with the effective nearest-neighbour coupling \( J_{eff} \) and the effective magnetic field \( H_{eff} \):

\[
Z(\beta, J, t, U, H_I, H_r) = A^N Z_I(\beta, J_{eff}, H_{eff}), \tag{2}
\]

where \( \beta = 1/T \) is the inverse temperature (we set the Boltzmann’s constant \( k_B = 1 \)) and \( N \) is the total number of the nodal lattice sites (the localized Ising spins). The explicit expressions of the mapping parameters \( A, J_{eff} \) and \( H_{eff} \) emerging in Eq. (2) can be obtained from the ‘self-consistency’ condition of the applied decoration-iteration transformation (see Eqs. (9) and (10) in Ref. [16]). At this stage, the exact calculation of the partition function \( Z \) of the spin-electron tetrahedral chain is formally completed, because the partition function \( Z_I \) of the spin-1/2 Ising linear chain in a magnetic field is known \([25, 26]\).

2.2. Magnetization, entropy and magnetic Gr"uneisen parameter

In this part, we present the exact solution for the Gibbs free energy \( G \), the total magnetization \( M \), the entropy \( S \) and the magnetic Gr"uneisen parameter \( \Gamma_H \) of the investigated spin-electron tetrahedral chain. The first three physical quantities immediately follow from the relation (3):

\[
G = -\frac{1}{\beta} \ln Z_I - \frac{N}{\beta} \ln A, \tag{3}
\]

\[
M = M_I + 2M_e = -\frac{\partial G}{\partial H_I} - 2\frac{\partial G}{\partial H_e} = \frac{1}{\beta} \ln Z_I + \frac{N}{\beta} \ln A + 2 \frac{\partial \ln Z_I}{\partial \beta} - 2N \frac{\partial \ln A}{\partial \beta}. \tag{4}
\]

\[
S = -\frac{\partial G}{\partial T} = \frac{\beta}{\beta} \frac{\partial G}{\partial \beta} = \ln Z_I + N \ln A - \beta \frac{\partial \ln Z_I}{\partial \beta} - N \beta \frac{\partial \ln A}{\partial \beta}. \tag{5}
\]

The partial derivatives of the functions \( \ln Z_I \) and \( \ln A \), appearing in Eqs. (4) and (5), satisfy the general equations:

\[
\frac{\partial \ln Z_I}{\partial x} = \frac{N}{2} \left[ \frac{1}{2} + \frac{s^2 - Q^2}{Q(c + Q)} \right] \frac{\partial \ln (W_{s} + W)}{\partial x}, \tag{6}
\]

\[
\frac{\partial \ln A}{\partial x} = \frac{1}{4} \frac{\partial \ln (W_{s} + W)}{\partial x} + \frac{1}{4} \frac{\partial \ln (W_{s} + W)}{\partial x} + \frac{1}{2} \frac{\partial \ln (W_0 + W)}{\partial x}, \tag{7}
\]

where \( s = \sinh(\beta H_{eff}/2) \), \( c = \cosh(\beta H_{eff}/2) \) and \( Q = \sqrt{\sinh^2(\beta H_{eff}/2) + \cosh^2(\beta H_{eff})} \). Forms of the functions \( W_s \), \( W_0 \) and \( W \) are listed in Eq. (10) of Ref. [16].

The so-called magnetic Gr"uneisen parameter \( \Gamma_H \), which can be calculated from the relation (see Ref. [27] for a recent review):

\[
\Gamma_H = -\frac{1}{C_H} \left( \frac{\partial M}{\partial T} \right)_H = -\frac{1}{T} \left( \frac{\partial S}{\partial T} \right)_H = -\frac{1}{T} \left( \frac{\partial T}{\partial H} \right)_S, \tag{8}
\]
It is worthwhile to remark that the FM and FRU phases also appear in the ground state of the antiferromagnetic counterpart of the model (see our preceding paper [13]). Thus, we present here just their eigenvectors and brief definitions for the sake of easy reference:

- The ferromagnetic (FM) phase:

\[
|\text{FM}\rangle = \prod_{k=1}^{N} |\uparrow\rangle_{c_k} \otimes \left( \frac{1}{\sqrt{3}} \left( c_{k,1}^\uparrow c_{k,2}^\uparrow + \omega c_{k,2}^\uparrow c_{k,3}^\uparrow + \omega^2 c_{k,3}^\uparrow c_{k,1}^\uparrow \right) |0\rangle \right),
\]

where \( \omega = e^{2i\pi/3} \) (\( i^2 = -1 \)). In this phase, the mobile electrons at each triangular cluster underlie a quantum superposition of three ferromagnetic states \( c_{k,1}^\uparrow c_{k,2}^\uparrow |0\rangle \), \( c_{k,2}^\uparrow c_{k,3}^\uparrow |0\rangle \), \( c_{k,3}^\uparrow c_{k,1}^\uparrow |0\rangle \) and the Ising spins localized at nodal lattice sites occupy the spin state \( \sigma^z = 1/2 \).

- The frustrated (FRU) phase:

\[
|\text{FRU}\rangle = \begin{cases} \prod_{k=1}^{N} |\uparrow\rangle_{c_k} \otimes \frac{1}{\sqrt{6}} \left[ \sin \varphi \left( c_{k,1}^\uparrow c_{k,2}^\uparrow + c_{k,2}^\uparrow c_{k,3}^\uparrow + c_{k,3}^\uparrow c_{k,1}^\uparrow \right) + \sqrt{2} \cos \varphi \sum_{j=1}^{3} c_{k,j}^\uparrow c_{k,j+1}^\uparrow |0\rangle \right] & (H = 0) \\ \prod_{k=1}^{N} |\uparrow\rangle_{c_k} \otimes \frac{1}{\sqrt{6}} \left[ \sin \varphi \left( c_{k,1}^\uparrow c_{k,2}^\uparrow + c_{k,2}^\uparrow c_{k,3}^\uparrow + c_{k,3}^\uparrow c_{k,1}^\uparrow \right) + \sqrt{2} \cos \varphi \sum_{j=1}^{3} c_{k,j}^\uparrow c_{k,j+1}^\uparrow |0\rangle \right] & (H > 0) \end{cases},
\]

where \( \varphi = \frac{\pi}{3} \left( U + 2t + \sqrt{(U + 2t)^2 - 32t^2} \right) \). In this phase, the mobile electrons from each triangular cluster show the quantum entanglement of
six intrinsic antiferromagnetic states \(c_{k1}^\dagger c_{k2}^\dagger |0\rangle\), \(c_{k2}^\dagger c_{k3}^\dagger |0\rangle\), \(c_{k3}^\dagger c_{k1}^\dagger |0\rangle\), \(c_{k1}^\dagger c_{k2}^\dagger |0\rangle\), \(c_{k2}^\dagger c_{k3}^\dagger |0\rangle\), \(c_{k3}^\dagger c_{k1}^\dagger |0\rangle\), and three non-magnetic ionic states \(c_{k1}^\dagger c_{k1}^\dagger |0\rangle\) \((j = 1, 2, 3)\) while the arrangement of the localized Ising spins depends on a presence of the external magnetic field: if \(H = 0\), the Ising spins are completely free to flip in arbitrary direction, while they are fully polarized into the field direction, if \(H \neq 0\).

In both Eqs. (11) and (12), the products run over all primitive unit cells, the state vector \(|\uparrow\rangle_{\sigma_i} (|\downarrow\rangle_{\sigma_i})\) determines the up (down) state of the Ising spin localized at \(k\)th lattice site and \(|0\rangle\) labels the vacuum state. As has been evidenced in Ref. [16], the above ground states are macroscopically degenerate, which consequently leads to a residual entropy \(S/3N = \ln 2^{1/3} \approx 0.231\) in both the phases. The FM phase is macroscopically degenerate due to chiral degrees of freedom of the mobile electrons, while the FRU phase exhibits a macroscopic degeneracy owing to a kinetically-driven spin frustration of the localized Ising spins caused by the antiferromagnetic alignment of the mobile electrons. Arbitrary but non-zero magnetic field tends to align the Ising spins into the field direction and thus, it cancels the macroscopic degeneracy of the FRU phase (and also the associated residual entropy \(S/3N = \ln 2^{1/3}\)). By contrast, the FM phase remains macroscopically degenerate in the whole parameter region.

### 3.2. Adiabatic (de)magnetization process

Now, let us turn to the discussion of the magnetocaloric properties of the investigated model. In Fig. 3 we depict isothermal changes of the entropy per one magnetic particle \(S/3N\) (recall that the system is composed of \(N\) Ising spins and 2\(N\) mobile electrons) under the field variation assuming the fixed Coulomb term \(U/|J| = 5.0\), the hopping parameter \(t/|J| = 1.5\) and various temperatures. As one can see from this figure, the entropy isothersms monotonously decrease from its maximum at \(H/|J| = 0\) upon the increasing magnetic field down to temperature \(T/|J| = 1.0\). Below \(T/|J| = 1.0\), the entropy exhibits non-monotonous dependencies as a function of the external magnetic field with a pronounced peak at the critical field \((10)\), at which the system undergoes a phase transition between the FRU and FM phases. Finally, the continuous entropy isothersms split into the isolated points with the coordinates [\(H/|J|, S/3N\) = \([0, \ln 2^{1/3})\), \([H/|J|, S/3N\) = \([H_c/|J|, \ln 3^{1/3}]\) and the lines \(S/3N = 0 (H < H_c), S/3N = \ln 2^{1/3} (H > H_c)\) when the temperature reaches the zero value.

In general, the residual entropy found in the frustrated magnetic systems and at critical points corresponding to the phase transitions between different magnetic structures gives a rise to an enhanced MCE accompanied by a relatively fast cooling of systems during the adiabatic (de)magnetization. To investigate the efficiency of the adiabatic cooling of the considered spin-electron system in these regions, we plot in Fig. 4 the magnetic Grüneisen parameter multiplied by the temperature \(TT_H\) versus the external magnetic field for the relatively low temperature \(T/|J| = 0.2\) and a few values of the parameters \(t/|J|\) and \(U/|J|\).

Evidently, the low-temperature \(TT_H\) curves depicted in this figure exhibit two local maxima at very low (but non-zero) magnetic field and slightly above the critical field \((10)\) of the zero-temperature phase transition FRU–FM in addition to the one local minimum slightly below \((10)\). The sign change of the \(TT_H\) product observed close to the critical field \((10)\) clearly indicates a rapid accumulation of the entropy due to a mutual competition between the neighbouring ground-state configurations (see e.g. the curves plotted for \(t/|J| = 1.5\) in Fig. 4a) and for \(U/|J| = 5\) in Fig. 4b) and compare them with the corresponding isothermal dependence of \(S/3N\) in Fig. 3. Furthermore, the peaks appearing around the field-induced phase transition FRU–FM are much higher than those observed at relatively small magnetic fields. For example, for \(t/|J| = 1.5\) and \(U/|J| = 3, 5, 10\) we have \(TT_H \approx 41.6, 19.8, 6.5\) at \(H/|J| \approx 2.7, 2.3, 1.8\) and \(TT_H \approx 15.3, 7.1, 2.1\) at \(H/|J| \approx 0.007, 0.014, 0.043\) (see Fig. 4b). It is thus clear that the cooling capability of the system during the adiabatic (de)magnetization is substantially higher (approximately three times) just above the critical field, where strong thermal excitations of the mobile electrons are present at relatively low temperatures due to breaking up the quantum superpositions of their up-down states, than that one at relatively small magnetic fields, where the Zeeman’s splitting of energy levels of the frustrated Ising spins takes place. Except to this behaviour, Fig. 4 also illustrates the effect of the hopping parameter and the on-site Coulomb repulsion on the enhancement of the MCE in the investigated model. It is quite evident from this figure that the adiabatic cooling rate of the system generally increases in the vicinity of the zero field and nearby the field-induced phase transition FRU–FM with increasing the kinetic term \(t/|J|\) (see Fig. 4a), while it decreases in these regions with increasing the Coulomb parameter \(U/|J|\) (see Fig. 4b).

To discuss the MCE in the considered spin-electron double-tetrahedral chain, we may alternatively investigate an adiabatic change of temperature of the model under the magnetic field variation. For this purpose, we present a density plot of the entropy as a function of the magnetic field and temperature for the fixed Coulomb term \(U/|J| = 5.0\) and the hopping param-
Figure 4: The magnetic Grüneisen parameter multiplied by the temperature $TT_\mu$ versus the magnetic field for the fixed temperature $T/|J| = 0.2$ and the set of parameters: (a) $U/|J| = 5.0$, $t/|J| = 1.0, 1.3, 1.5$, (b) $t/|J| = 1.5$, $U/|J| = 3, 5, 10$.

Figure 5: A density plot of the entropy as a function of the magnetic field and temperature by assuming the fixed Coulomb term $U/|J| = 5.0$ and the hopping term $t/|J| = 1.5$. The displayed curves correspond to isentropy lines, namely, $S/3N = 0.01, 0.1, 0.2$ (black broken curve), $S/3N = \ln 2^{1/3}$ (white broken curve), $S/3N = 0.24, 0.26, \ldots, 0.4$ (black solid curves) and $S/3N = \ln 3^{1/3}$ (white solid curve).

to two macroscopically degenerate ground states (FRU and FM), which can also be found in the antiferromagnetic counterpart of the model [16]. We have shown that the macroscopic degeneracy of the FRU phase arising due to the kinetically-driven frustration of the localized Ising spins as well as the macroscopic degeneracy of the system at the field-induced phase transition between the FRU and FM phases perfectly manifest themselves in the enhanced MCE during the adiabatic (de)magnetization. It has been evidenced that the cooling capability of the system during the adiabatic (de)magnetization is approximately three times higher nearby the phase transition FRU–FM, where strong thermal excitations of the mobile electrons are present at relatively low temperatures due to breaking up the quantum superpositions of their up-down states, than that one at relatively small magnetic fields, where the Zeeman’s splitting of energy levels of the frustrated Ising spins takes place.

4. Conclusions

The present Letter deals with the ground-state and magneto-caloric properties of the double-tetrahedral chain, where the nodal lattice sites occupied by the localized Ising spins regularly alternate with three equivalent lattice sites available for two mobile electrons. Based on the exact solution of the model presented in Ref. [16], we have analytically derived exact results for the basic thermodynamic quantities, such as the Gibbs free energy, the total magnetization, the entropy and the magnetic Grüneisen parameter of the system. By considering the ferromagnetic exchange interaction ($J < 0$) between the mobile electrons and their nearest Ising neighbours, we have found

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