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Thermodynamics of spin ice on an antiperovskite lattice in the cluster approximation

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Low-temperature thermodynamic properties of spin ice have been studied for compounds with the structure of antiperovskite containing rare-earth ions with the general chemical formula $ReMe$O (where Re — is a rare-earth element, Me — is a divalent metal). The calculations were carried out in the cluster approximation. The cases of undistorted and distorted ORe_6 octahedron are discussed. In the case of an undistorted octahedron in the absence of an external magnetic field, the ground state of the system is infinitely degenerate. When an external magnetic field is applied, anomalies in the temperature dependences of heat capacity, entropy and magnetization are detected. In the case of a distorted octahedron and assuming that this distortion leads to the energy efficiency of two of the sixty-four configurations, it is obtained that there is a phase transition in the system of magnetic rare-earth ions.

Keywords: phase transitions, magnetism, competing interactions.

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1. Introduction

Thermodynamic properties of geometrically frustrated magnetic systems have been attracting attention of researchers during decades. In such systems, the ground state has a high degree of degeneracy resulting in residual entropy at 0 K and often to unusual behavior of thermodynamic variables in the low temperature region. After discovery of the spin ice state in compounds with the pyrochlore structure containing rare-earth metal ions [1,2], the interest in the study of geometrically frustrated magnets has been grown considerably and by now there is a lot of studies devoted to the investigation of spin ice properties (see, for example, reviews [3,4]. In the pyrochlore structure, the rare-earth ions form a lattice of tetrahedra connected in their vertices, and the spin ice state corresponds to the states where two magnetic moments of a rare-earth ion in each tetrahedron are directed inside the tetrahedron and to moments are directed outside (two-in-two-out). thermodynamic properties of the Ising model). So-called magnetic monopoles occur in the excited states and such states are referred to as the Coulomb phase. Existence of the Coulomb phase is not limited by the pyrochlore structure: it was found, or example, in two-dimensional systems such as the artificial spin ice [5] and kagome ice [6].

A recent paper [7] discusses the possibility of spin ice state implementation in three-dimensional systems using the case of compounds with chemical formula MeORe_3 (where Re is the rare earth element, Me is the bivalent metal) with the antiperovskite structure where the rare-earth metal ions are in the octahedron vertices, and the three-in-three-out states correspond to the spin ice state. The authors of [7] study the thermodynamic properties of the Ising model with the exchange and dipole-dipole interactions by the Monte Carlo method.

In compounds with the antiperovskite structure containing rare-earth ions, a three-dimension lattice of octahedra connected in their vertices. Since the spins of f-electrons of rare earth elements have a high magnetic moment, they may be treated as classical variables and, at rather low temperatures, their behavior is described as the Ising doublet directed along the axis connecting the octahedron center and vertex. Geometrical frustration is caused, on the one hand, by the noncollinearity of the crystal field and effective magnetic interaction and, on the other hand, by the fact that the Ising doublet axes in the lattice cell are fixed and are different, as a result each octahedron has eight possible configurations with the sane energy which corresponds to the minimum free energy and, thus, the ground state of the magnetic moment system of rare-earth ions is endlessly degenerate. Description of thermodynamic properties of systems with competing interactions by the mean field approximation results in qualitatively wrong results, and for the description of such systems, approximations shall be used where the interaction competition is more or less considered explicitly. One of such approximations is the approximation of clusters.

Investigation of thermodynamic properties in the magnetic rare-earth ion system in the antiperovskite structure as well as the possibilities of magnetic ordering in this system in case of distorted octahedron ORe_6 in the cluster approximation is the aim of this study.

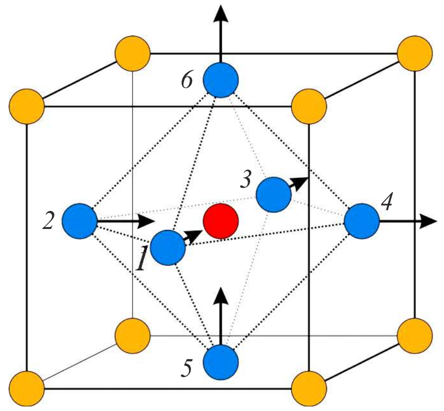

Figure 1. antiperovskite structure $MeORe_3$. In the cube vertices — Me, in the center — oxygen, in the center of faces — rare earth Re.

2. Free energy in the six-particle cluster approximation

Only the magnetic system of rare-earth ions will be discussed below,

Figure 1 shows the antiperovskite structure in the highly symmetric cubic phase $Pm\bar{3}m$ with rare-earth ions in the octahedron vertices (designated by numbers from $1-6$) and the Ising doublet vectors in the lattice cell. To describe the thermodynamic properties of the model, the variational cluster method [8,9] is used and the simplest cluster of six spins will be addressed. The ground state of the magnetic rare earth element ion system may be considered as vertex with one of the possible 64 octahedron spin configurations. In the crystal with cubic symmetry $Pm\bar{3}m$, 20 configurations „allowed by the ice rule", i. e. three-in-three-out, are divided into two groups (8 and 12 configurations) with the same configuration energy inside the group. Thirty configurations (15 four-in-two-out with positive magnetic charge and 15 two-in-four-out with negative magnetic charge) are divided into three groups with the same energy inside the group. Twelve configurations have the same energy (6 five-in-one-out with positive magnetic charge $+2$ and 6 one-in-five-out with negative magnetic charge -2). And finally, two configurations (1 all-in with positive magnetic charge $+3$ and 1 all-out with negative magnetic charge -3).

In case of distorted octahedron in the crystal with symmetry other than cubic, degeneracy is removed and a phase transition into the ordered state is possible in the magnetic ion system.

Assume $\sigma^z = \pm 1$ for two possible magnetic moment directions of the rare-earth ion inside and outside the octahedron. Then the Hamiltonian of the model may be written as the Ising model Hamiltonian:

$$\mathcal{H} = \sum_{ij} J_{i,j}\sigma_i^z\sigma_j^z - H\sum_i \sigma_i^z. \quad (1)$$

Assume $\sigma_1^z = \sigma_2^z = \sigma_3^z = \sigma_4^z = \sigma_5^z = \sigma_6^z = 1$ for the configuration in Figure 1. Then, in the cluster approximation, taking into account the external filed, the cluster and single-particle Hamiltonians are written as

$$\begin{aligned}\mathcal{H}_6 = J_1(&\sigma_1^z\sigma_2^z - \sigma_1^z\sigma_4^z + \sigma_1^z\sigma_5^z - \sigma_1^z\sigma_6^z - \sigma_2^z\sigma_3^z + \sigma_2^z\sigma_5^z \\ &- \sigma_2^z\sigma_6^z + \sigma_3^z\sigma_4^z - \sigma_3^z\sigma_5^z + \sigma_3^z\sigma_6^z - \sigma_4^z\sigma_5^z + \sigma_4^z\sigma_6^z) \\ &- J_2(\sigma_1^z\sigma_3^z + \sigma_2^z\sigma_4^z + \sigma_5^z\sigma_6^z) \\ &- \left(\frac{\varphi}{2} + h\right)(\sigma_1^z + \sigma_2^z + \sigma_3^z + \sigma_4^z + \sigma_5^z + \sigma_6^z);\end{aligned}$$

$$\mathcal{H}_1 = (\varphi + h)\sigma_1^z. \quad (2)$$

Expression (2) includes the external magnetic field oriented along the spatial diagonal of the cubic cell $h = g\mu_B sH$ (g — g-factor, μ_B — Bohr magneton, s — rare-earth ion spin, and the direction cosines of the magnetic moments of the cluster ions, which are the same in this case, are included in h). The average energy per vertex is written as

$$E = \langle\mathcal{H}_6\rangle - 3\langle\mathcal{H}_1\rangle. \quad (3)$$

In (2) φ is the self-consistency field applied to the spin in the lattice. In the antiperovskite structure, rare-earth ion octahedra are connected in their vertices with each ion surrounded by ten ions of the connected octahedra. In the single-particle Hamiltonian, the ion is exposed to a full field from the ions of two connected octahedra. In the cluster Hamiltonian, interaction of each rare-earth ion with four ions with constant J_1 and with one ion with constant J_2 is considered accurately; interaction with the remaining adjacent ions is considered by the self-consistency field which is twice weaker in this case.

To describe the average energy (3) in the cluster approximation, the density matrices of the ρ_k k-th class are described as $\rho_k = \text{const}\cdot\exp(-\beta\mathcal{H}_k)$, where $\mathcal{H}_k$ is the cluster $\mathcal{H}_6$ and single-particle $\mathcal{H}_1$ Hamiltonians calculated in (2), $\beta = 1/T$ ($k_B = 1$). Free energy is calculated by integration with respect to β of the relation $E = \partial(\beta F)/\partial\beta$

$$\beta F = -\ln Z_6 + 3\ln Z_1, \quad (4)$$

where Z_6 and Z_1 are cluster and single-particle partition functions. In case of cubic symmetry Z_6 within the monomial factor, $\exp(3\beta J_2)$ and Z_1 are written as

$$\begin{aligned}Z_6 = 2\big(&\cosh(3\beta\varphi + 6\beta h) + 3\cosh(\beta\varphi + 2\beta h) \\ &+ 6K^4\cosh(\beta\varphi + 2\beta h) + 6LK\cosh(2\beta\varphi + 4\beta h) \\ &+ 6LK + 3LK^5 + 6L^4\cosh(\beta\varphi + 2\beta h) + L^9K^{-3}\big);\end{aligned}$$

$$Z_1 = 2\cosh(\beta\varphi + \beta h);$$

$$K = \exp\left(-\frac{\beta v}{4}\right), \quad L = \exp\left(-\frac{\beta w}{4}\right),$$

$$v = 4J_2 - 4J_1, \quad w = 4J_2 + 4J_1. \quad (5)$$

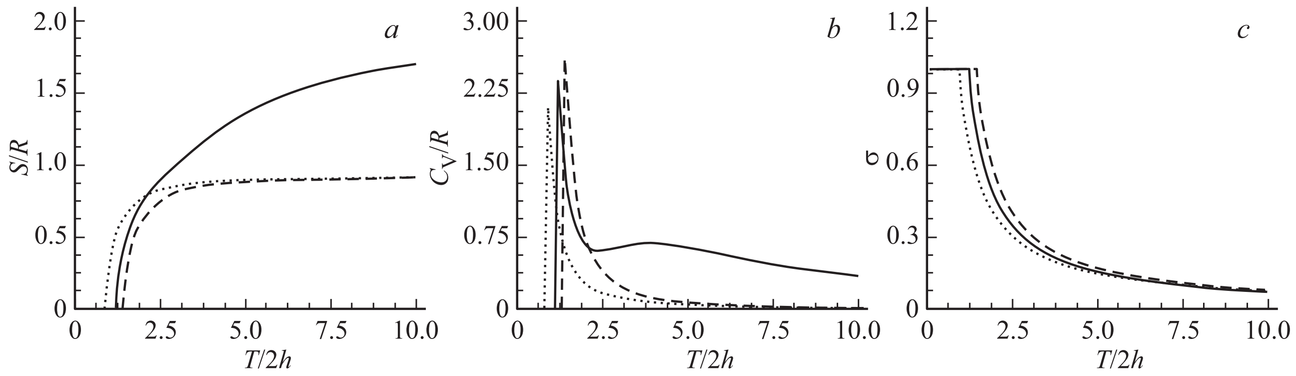

Figure 2. temperature dependences *a*) of entropy, *b*) heat capacity and *c*) average $\langle\sigma^z\rangle$ in case of cubic symmetry in the applied external field; dots — $w/2h \to \infty$, $v/2h = 0$; dashed line — $w/2h \to \infty$, $v/2h = 0.5$; solid curve — $w/2h = 4.5$, $v/2h = 0.5$.

Field φ is derived from the minimum free energy condition $\partial F/\varphi = 0$ and is defined by equation

$$\Big(\sinh(3\beta(\varphi + 2h)) + \sinh(\beta(\varphi + 2h)) + 2K^4 \sinh(\beta(\varphi + 2h)) + 2LK \sinh(2\beta(+2h)) + 2L^4 \sinh\big(\beta(\varphi + 2h)\big)\Big) / \big(\cosh(3\beta\varphi + 6\beta h) + 3\cosh(\beta\varphi + 2\beta h) + 6K^4 \cosh(\beta\varphi + 2\beta h) + 6LK \cosh(2\beta\varphi + 4\beta h) + 6LK + 3LK^5 + 6L^4 \cosh(\beta\varphi + 2\beta h) + L^9K^{-3}\big) = \sinh(\varphi + h)/\cosh(\varphi + h). \tag{6}$$

The average $\langle\sigma^z\rangle$ is calculated by

$$\langle\sigma^z\rangle = \tanh\beta(\varphi + h). \tag{7}$$

Entropy and specific heat capacity are calculated by

$$S = (-\partial F/\partial T); \quad C_V = -T(\partial^2 F/\partial T^2). \tag{8}$$

Expressions (4)−(8) determine the system thermodynamics.

In case when the crystal symmetry is lower than the cubic symmetry, octahedron ORe_6 is distorted, degeneracy is removed and a phase transition into the ordered state is possible in the magnetic ion system. The simplest degeneracy removal case will be addressed here. Assume that due to the octahedron distortion, two of twelve „neutral“ three-in-three-out configurations have the lowest energy which will be assumed as equal to zero. To minimize the number of unknown parameters of the model and for simplicity, assume that the energies of the remaining configurations will vary by the same value and denote this energy by ε. The energies of one-, two-and three-„charged“ configurations will be assumed the same as for the cubic symmetry. In this case, expression (5) and equation (6) are written as

$$Z_6 = 2\big(\cosh(3\beta\varphi + 6\beta h) + 3G\cosh(\beta\varphi + 2\beta h) + 6GK^4 \cosh(\beta\varphi + 2\beta h) + 6LK \cosh(2\beta\varphi + 4\beta h) + 6LK + 3LK^5 + 6L^4 \cosh(\beta\varphi + 2\beta h) + L^9K^{-3}\big); \tag{9}$$

$$\Big(\sinh\big(3\beta(\varphi + 2h)\big) + G\sinh\big(\beta(\varphi + 2h)\big) + 2GK^4 \sinh\big(\beta(\varphi + 2h)\big) + 2LK \sinh\big(2\beta(\varphi + 2h)\big)\Big) + 2L^4 \sinh\big(\beta(\varphi + 2h)\big)\Big) / \big(\cosh(3\beta\varphi + 6\beta h) + 3G\cosh(\beta\varphi + 2\beta h) + 6GK^4 \cosh(\beta\varphi + 2\beta h) + 6LK \cosh(2\beta\varphi + 4\beta h) + 6LK + 3LK^5 + 6L^4 \cosh(\beta\varphi + 2\beta h) + L^9 \cdot K^{-3}\big) = \sinh(\varphi + h)/\cosh(\varphi + h), \tag{10}$$

where $G = \exp(-\beta\varepsilon)$.

3. Results

Let us first discuss the cubic symmetry case. First of all, note that equation (6) without the field $H = 0$ has a unique solution $\varphi = 0$ at all temperatures, i.e. without field, the system of magnetic moments of rare-earth ions is endlessly degenerated at $T = 0$ K. When $J_1 = J_2$ in (2), i.e. at $v = 0$, all 20 three-in-three-out configurations have the same energy. Note also that, if excited configurations with magnetic charge are prohibited in this case, i.e. $w \to \infty$ is assumed, than from (4) follows the result for the residual Pauling entropy: $F = -T \cdot \ln 5/2$, $S = \ln 5/2$.

Now let us discuss the results at non-zero field H.

When „charged“ configurations are prohibited $w \to \infty$, the dependences of heat capacity, entropy and average $\langle\sigma^z\rangle$ on temperature T are shown in Figure 2 for two values of v.

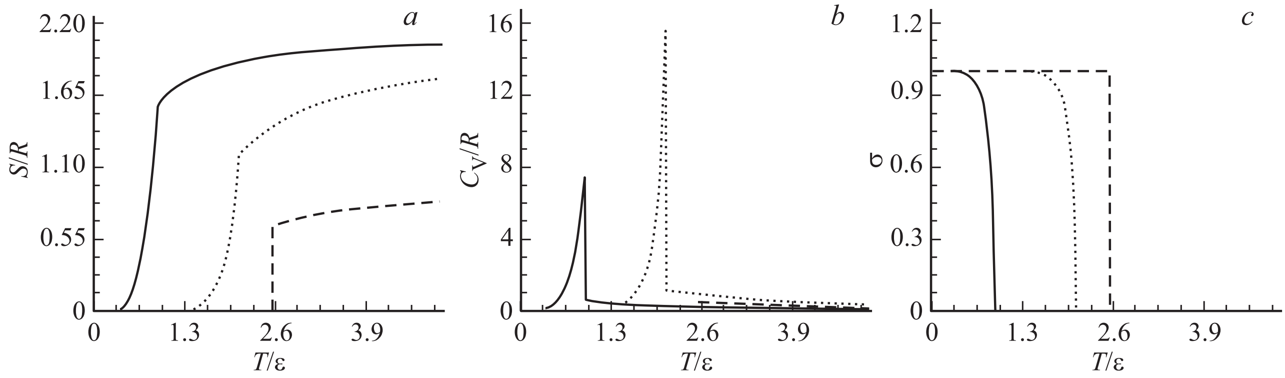

Figure 3. Temperature dependences of a) entropy, b) heat capacity and c) order parameter $\langle\sigma^z\rangle$ for distorted octahedron ORe_6; dashed line — $w/\varepsilon\to\infty$, $v/\varepsilon=0.9$; solid line — $w/\varepsilon=0.5$, $v/\varepsilon=0.9$; dots — $w/\varepsilon=4.5$, $v/\varepsilon=0.9$.

Dependence of the transition temperature and entropy change $\Delta S=S(T_c)-S(0)$ (per formula unit) on v/ε and w/ε

	$w/\varepsilon\to\infty$		$w/\varepsilon=4.5$		$w/\varepsilon=2.5$		$w/\varepsilon=1.5$		$w/\varepsilon=0.5$	
v/ε	T_c/ε	$\Delta S/R$	T_c/ε	$\Delta S/R$	T_c/ε	$\Delta S/R$	T_c/ε	$\Delta S/R$	T_c/ε	$\Delta S/R$
0	0.91	0.83	0.89	0.94	0.79	1.30	0.64	1.54	0.35	1.55
0.1	1.14	0.81	1.09	1.04	0.95	1.40	0.79	1.59	0.47	1.62
0.3	1.57	0.77	1.41	1.06	1.20	1.43	1.00	1.56	0.64	1.63
0.5	1.89	0.72	1.65	1.10	1.40	1.42	1.17	1.52	0.73	1.62
0.7	2.22	0.68	1.87	1.13	1.56	1.39	1.31	1.48	0.84	1.62
0.9	2.54	0.64	2.07	1.19	1.71	1.36	1.43	1.45	0.91	1.62

It can be seen that, depending on the heat capacity for $v=0$, there is a peak at a temperature approximately equal to $2h$. This temperature corresponds to the saturation temperature in the dependence of the average $\langle\sigma^z\rangle$ on temperature. With finite value of v, the qualitative behavior of thermodynamic values remains the same as with $v=0$, but the abnormal behavior peak moves towards high temperatures as shown in Figure 2.

With finite energy of „charged" states w, besides the abnormal behavior mentioned above, additional abnormalities occur in the thermodynamic parameter dependences which are associated with the excitation of these „charged" states in a certain temperature region. Figure 2 shows the dependences of heat capacity, entropy and average $\langle\sigma^z\rangle$ on temperature for $w/2h=4.5$. It can be seen that at a temperature about $2h$, behavior of thermodynamic variables does not differ from the case of $w\to\infty$, however, at high temperatures, additional washed-out abnormality occurs in the dependence of heat capacity on temperature, which is associated by the excitation of „charged" states. The maximum temperature of this abnormality is defined by the value of w.

Consider the case of distorted octahedron and, therefore, the phase transition into the ordered state at the external field equal to zero. In expressions (9) and (10), assume $h=0$. The equation for the temperature instability of the disordered phase T_c is derived from equation (10) by expansion in φ with an accuracy up to the first order:

$$2G_c+4G_cK_c^4+4L_cK_c+3L_cG_cK_c^5+4L_c^4+L_c^9K_c^{-3}=2, \tag{11}$$

where G, L, K are calculated in (5) with $T=T_c$.

When the configurations with magnetic charge ($w\to\infty$) are prohibited, the instability temperature of the disordered phase is derived from $G_c+2G_cK_c^4=1$. The same temperature is the phase transition temperature at which the order parameter $\langle\sigma^z\rangle$ is changed stepwise from zero to one and the susceptibility becomes infinite. The minimum free energy of the system which in this case is written as

$$\beta F=-\ln\Big(\big(\cosh(3\beta\varphi)+3G\cosh(\beta\varphi)(1+2K^4)\big)/4\cosh(\beta\varphi)\Big),$$

for $T\geq T_c$ corresponds to $\varphi=0$, and for $T\leq T_c$ $\varphi=\infty$.

With $J_1=J_2$ in (2), i.e. at $v=0$, and with $w\to\infty$, the transition temperature is equal to $T_c=\varepsilon/\ln 3$.

It should be emphasized that the thermodynamic properties of the system in this case coincide with the Slater model properties [9], except T_c which is equal to $\varepsilon/\ln 2$ in the Slater model.

The temperature dependence of heat capacity, entropy and order parameter $\langle\sigma^z\rangle$ for several finite values w is shown in Figure 3.

With finite energy value of „charged" states, the phase transition becomes the second order transition. The table lists T_c values calculated by (7) for various values of v/ε and w/ε.

4. Conclusion

The study used a simple model to investigate thermodynamic properties of the spin ice in the antiperovskite structure where the rare-earth metal ions occupy the vertices of the octahedron with the oxygen ion in the center. Thermodynamic functions are calculated in the cluster approximation using the smallest cluster of six particles considering the spin ice state and magnetically charged states in the system of magnetic moments of the rare earth ions. Two undistorted and distorted octahedron cases are addressed.

The following result is obtained.

In case of undistorted octahedron, 8 states with three-in-three-out configuration are assumed to have the lowest and the same energy. Another 12 states with three-in-three-out configuration also have the same energy. In the absence of the external magnetic field, the system ground state is endlessly degraded. When the external magnetic field is applied, abnormalities in the temperature dependences of heat capacity and entropy were found. Abnormal behavior of the thermodynamic parameters at a temperature approximately equal to the double external filed strength is associated with full order established in the magnetic ion system at this temperature. In the temperature dependence of heat capacity at higher temperatures, the second abnormality is observed which is associated with the excitation of „charged" magnetic configurations at these temperatures.

In case of distorted octahedron and on the assumption that the distortion results in energetical benefit of two of eight three-in-three-out configurations, while the rest six configurations have the same energy ε, it is also assumed that the energy of rest twelve three-in-three-out configurations increases by ε in this case. In this case the rare-earth ion system has a phase transition to an ordered state at a finite temperature. When the „charged" configurations are prohibited and the energies of 18 three-in-three-out configurations are equal, this transition occurs at $T_c = \varepsilon/\ln 3$ with susceptibility becoming infinite and the order parameter jumping to the maximum. Note that this transition is similar to the transition in the six-vertex model (Slater model) for which an accurate solution is known and the transition and order parameter jump temperatures calculated in the four-particle cluster approximation coincide with the accurately calculated values.

At the finite energy of the „charged" configurations, the phase transition to the ordered state is the second-order transition.

Conflict of interest

The author declares that he has no conflict of interest.

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