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Modeling of magnetic and magnetocaloric properties of $La_{0.7}Ba_{0.3}MnO_3$ manganites by Monte Carlo method

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In the work the temperature dependence of magnetization, entropy changes, and the Curie temperature of $La_{0.7}Ba_{0.3}MnO_3$ using Monte Carlo method and Heisenberg model were investigated. We used the magnetic exchange parameters from the first-principles calculations. In the simulation, magnetic Mn^{3+} and Mn^{4+} ions are described by classical Heisenberg spins, while oxygen, lanthanum and calcium ions are considered as non-magnetic. Mn magnetic ions are distributed on *R*3*c* lattice according to the perovskite structure of the manganite. The Curie temperature and magnetocaloric effect values obtained during the theoretical simulations are in a good agreement with the experimental data.

При помощи метода Монте-Карло и модели Гейзенберга получена температурная зависимость намагниченности, изменение энтропии и определена температура Кюри манганитов лантана $La_{0.7}Ba_{0.3}MnO_3$. Для этих целей использованы значения интегралов обменных констант, полученных с помощью первопринципных расчетов. При моделировании магнитные Mn^{3+} и Mn^{4+} ионы описываются классическими спинами Гейзенберга, а кислород, лантан и ионы кальция считаются немагнитными. Магнитные ионы марганца распределены в *R*3*c* решетке в соответствии со структурой перовскита. Температуры Кюри и значения магнитокалорического эффекта, полученные в ходе теоретического моделирования, хорошо согласуются с экспериментальными данными.

1. Introduction

The magnetic refrigeration technology attracts the increasing attention of researchers. The magnetocaloric effect (MCE) is a magneto-thermodynamic phenomenon in which a reversible change in temperature of a suitable material is caused by exposing the material to a changing magnetic field [1]. It has great importance in the technology of magnetic refrigeration. Among the various alternative technologies that could be used in refrigeration devices, the increasing attention of researchers in the world attracts the technology of magnetic refrigeration [2–5]. The magnetic materials with large values of magnetocaloric effect can be applied as work substances in magnetic cooling devices such as industrial and household refrigerators, air conditioners, heat pumps, etc [4]. Until recently, the rare-earth metal Gd is regarded as the most promising material for use as a working one in magnetic cooling devices [6]. Because the fact that the cost of gadolinium is high enough in last time more attention has been focused on finding new materials that are cheaper and have a large MCE. It was found that such compounds include Ni–Mn–Ga, Mn–As–Sb, La–Fe–Si, rare earth manganites [3,4, 7–11]. Manganites have the general formula: $R_{1-x}M_xMnO_3$, where R — trivalent rareearth elements such as La, Pr, Eu, Gd, etc., M — divalent alkali ions such as Ba, Ca or Na, K, Ag, and etc. In recent years, perovskite manganites have been intensively studied. These compounds allow us to vary the temperature of phase transitions in a wide range of temperatures and thus realize a wide temperature range of the MCE [2].

Presence of experimental works on research of phase transitions and MCE in perovskite manganites leads to necessity of the analysis of experimental results by means of various theoretical models. For today in scientific publications there is a big number of works in which the theoretical models are discussed, allowing to describe phase transitions and MCE in various magnetic materials. However the theoretical works allowing to describe MCE in manganites by means of Monte Carlo method are practically absent.

In our work using the computed values of the magnetic exchange interactions by the first-principles calculations and using the Heisenberg's Hamiltonian we present Monte Carlo calculations of the temperature dependence of magnetization, entropy changes, and the Curie temperature of $La_{0.7}Ba_{0.3}MnO_3$.

2. Model and simulation

In this paper the values of the magnetic exchange interactions were calculated using the SPR-KKR (Spin Polarized Relativistic Korringa-Kohn-Rostoker code) package [12]. Korringa-Kohn-Rostoker code is based on the Green's functions as opposed to Bloch wave functions and eigenvalues. The Heisenberg exchange parameters were calculated using the theory of Lichtenstein et al. [13], where the exchange interactions between a pair of spins is calculated using a classical Heisenberg Hamiltonian. The chemical disorder has been treated by the single site coherent potential approximation (CPA). The maximum number of CPA iterations and the CPA tolerance were set to 20 and 0.01 mRy, respectively. The first step in these calculations was to calculate the self-consistent potential (SCF). The maximum number of SCF iterations was taken to 200. After the self-consistent potential was calculated it was used to simulate the Heisenberg's magnetic exchange coupling parameters using Spin-Polarized Scalar-Relativistic (SP-SREL). Interactions were taken into account in the first and second coordination sphere. It is known that in manganites at low temperatures is a series of structural and magnetic phase transitions. For example, such transitions occur in $La_{0.7}Ba_{0.3}MnO_3$ [14]. It is shown that, in the manganites two structural phases can be observed: low-temperature Imma and high-temperature $R3c$. In our work, we calculated the exchange constants for the $R3c$ phases of $La_{0.7}Ba_{0.3}MnO_3$ manganite.

Table. The calculated values of the integrals of the exchange interaction for $La_{0.7}Ba_{0.3}MnO_3$

Second coordination sphere		First coordination sphere	
	Jex (meV)		*Jex* (meV)
J_1	0.06	J_1	3.05
J_2	0.06	J_2	3.07
J_3	0.06	J_3	3.05
J_4	0.06	J_4	2.63
J_5	0.06	J_5	2.66
J_6	0.06	J_6	2.63

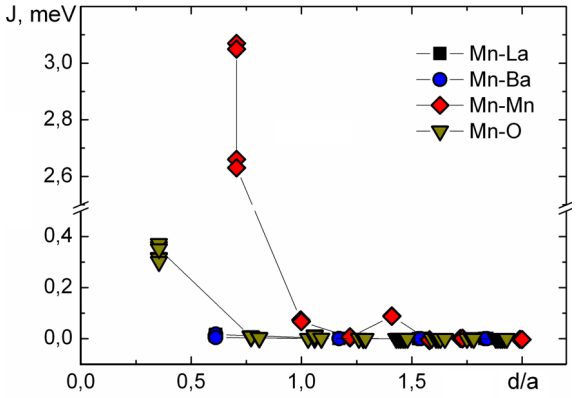

Fig. 1. *Ab initio* magnetic exchange interactions as a function of the distance d/a between pairs of atoms i and j (in units of the lattice constant a).

Manganite $La_{0.7}Ba_{0.3}MnO_3$ crystallizes in a perovskite structure in which trivalent Mn^{3+} and tetravalent Mn^{4+} ions are distributed in to $R3c$ lattice, having coordination number of six in the first coordination sphere and having also coordination number of six in the second coordination sphere. Table presents the results of *ab initio* calculations of the magnetic exchange interactions J_{ij}.

Fig. 1 shows the dependence of magnetic exchange interactions on the interatomic distance.

3. Monte Carlo study

In our simulation model magnetic Mn^{3+} and Mn^{4+} ions are described by classical Heisenberg spins, while oxygen, lanthanum and calcium ions are considered as non-magnetic. The Monte Carlo simulations have been carried out employing the standard Metropolis algorithm. The number of sites used in the simulations was $N = 15^3$. The number of Monte Carlo steps is $5 \cdot 10^5$. We started the simulations in the ferromagnetic

phase. The energy H of the system and the order parameters m were averaged for 400 Monte Carlo steps. In order to obtain equilibrium values of H and m the first 10^4 Monte Carlo steps were discarded.

At calculation we used the interactions within first and second coordination sphere. The Hamiltonian used in this work is

$$E = -\sum_{ij} J_{ij}\mathbf{S}_i\mathbf{S}_j - g\mu_B H\sum_i S_{zi},$$

where J_{ij} are the exchange interaction parameters, $S_i = \{S_x, S_y, S_z\}$ are spins of manganese ions, and H is the applied magnetic field. S_i takes the values 2 for Mn^{3+} (eg') and Mn^{3+} (eg) or 3/2 for Mn^{4+} ($d3$) according to the electronic configuration of ions [15]. μ_B is the Bohr magneton and g is the Lande factor.

The relative magnetization was calculated by the following formula:

$$m = \sqrt{S_x^2 + S_y^2 + S_z^2}.$$

Thermodynamic properties such as heat capacity (C), lattice specific heat (C_{lat}), magnetic specific heat (C_{mag}), entropy (S), isothermal entropy change (ΔS) were calculated using the following standard expressions [16]:

$$C_{mag} = \frac{1}{k_B T^2}[<E^2> - <E>^3],$$

$$C_{lat} = 9RN_i\left\{4\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} dx\frac{x^3}{e^x - 1} - \left(\frac{\theta_D}{T}\right)\frac{1}{e^{\theta_D/T} - 1}\right\},$$

$$C = C_{lat} + C_{mag},$$

$$S = \int_{T_1}^{T_2}\frac{C}{T}dT, \quad \Delta S = S_H - S_0, \quad \Delta T = -T\frac{\Delta S}{C},$$

where N_i is the number of ions per formula unit and Θ_D is the Debye temperature. S_H and S_0 denote the entropy in presence of a magnetic field H and in zero field, respectively. R is the gas constant, k_B is the Boltzmann constant.

4. Results and discussion

In our previous work [17] we experimentally investigated the properties of $La_{0.7}Ba_{0.3}MnO_3$. Lanthanum manganites were prepared by solid-state reaction technique. Temperatures of phase transition were experimentally found. Magnetic and magnetocaloric properties in samples were investigated. It was shown, that the Curie temperature is 324 K for $La_{0.7}Ba_{0.3}MnO_3$. It was also revealed, that the large adiabatic change of temperature (ΔT_{ad}) at magnetic field change takes place near the temperature of magnetic phase transition. From these results $La_{0.7}Ba_{0.3}MnO_3$ material was strongly suggested to be used for magnetic refrigeration equipment working near and above room temperature.

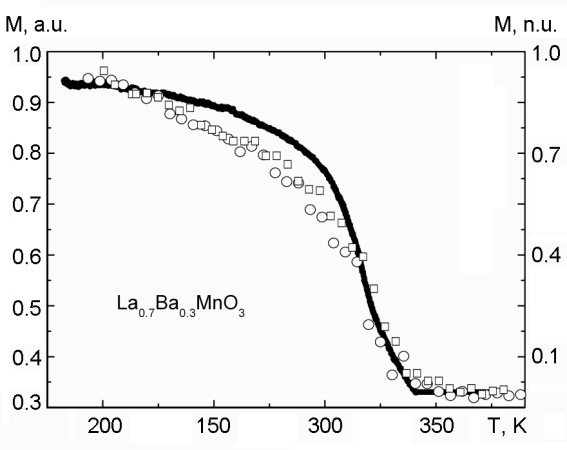

Fig. 2. Temperature dependence of magnetization for $La_{0.7}Ba_{0.3}MnO_3$. Here the empty squares and circles are the results of theoretical modeling with account of the exchange interactions in the first and second coordination spheres and in the first coordination sphere only, respectively. Filled symbols present the experimental measurements [17].

Fig. 2 shows the results of theoretical modeling of the temperature dependence of magnetization for $La_{0.7}Ba_{0.3}MnO_3$.

It is seen from Fig. 2 that the Curie temperature for $La_{0.7}Ba_{0.3}MnO_3$ obtained during our theoretical simulations agrees well with experimental data. Our calculations also shown that the magnetization calculated with account of the exchange interactions in two coordination spheres was more close to the experimental one.

In Fig. 3 we present the calculated magnetic entropy change for $La_{0.7}Ba_{0.3}MnO_3$ compound upon magnetic field variation from 0 to 2 T. It can be seen that the maximal MCE is observed at the Curie point.

Fig. 4 shows the results of theoretical modeling of adiabatic temperature change at changing of magnetic field from 0 to 2 T for $La_{0.7}Ba_{0.3}MnO_3$. As seen from Fig. 4 the magnetocaloric effect obtained during the

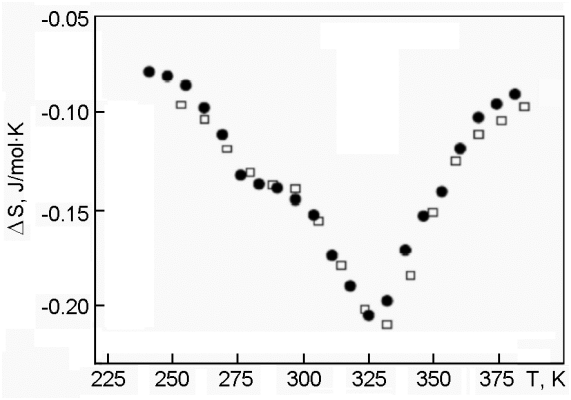

Fig. 3. Calculated magnetic entropy change for $La_{0.7}Ba_{0.3}MnO_3$ upon magnetic field variation from 0 to 2 T. Here empty and filled symbols are the results of theoretical modeling with account of the exchange interactions in the first and second coordination spheres and in the first coordination sphere only, respectively.

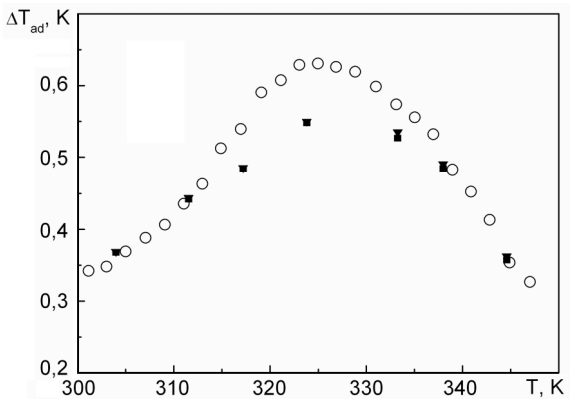

Fig. 4. Adiabatic temperature change for $La_{0.7}Ba_{0.3}MnO_3$. Here the filled triangular and squares are the results of theoretical modeling with account of the exchange interactions in the first and second coordination spheres and in the first coordination sphere only, respectively. Empty symbols present the experimental measurements [17].

theoretical simulations agrees well with the experimental data.

5. Conclusions

In this paper the values of the magnetic exchange interactions were calculated using SPR-KKR package with account of the exchange interactions in the first two coordination spheres. Using these interactions we calculated the magnetocaloric effect and the temperature dependence of magnetization for $La_{0.7}Ba_{0.3}MnO_3$ by Monte Carlo simulations. The theoretically calculated adiabatic temperature change and the Curie temperature are in a good agreement with the available experimental data. The present Monte Carlo calculations can also be used for calculating the magnetocaloric properties for other perovskite manganese.

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Дослідження магнітних і магнітокалоричних властивостей манганітів лантану $La_{0,7}Ba_{0,3}MnO_3$ методом Монте-Карло

О.Павлухіна, В.Бучельніков, В.Соколовській

За допомогою методу Монте-Карло і моделі Гейзенберга отримано температурну залежність намагніченості, зміну ентропії і визначено температуру Кюрі манганітів лантану $La_{0,7}Ba_{0,3}MnO_3$. Для цих цілей використано значення інтегралів обмінних констант, отриманих за допомогою первопрінціпних розрахунків. При моделюванні магнітні Mn^{3+} і Mn^{4+} іони описуються класичними спинами Гейзенберга, а кисень, лантан і іони кальцію вважаються немагнітними. Магнітні іони марганцю розподілені в *R3c* решітці відповідно до структури перовскіту. Температури Кюрі і значення магнітокалоричного ефекту, отримані в ході теоретичного моделювання, добре узгоджуються з експериментальними даними.