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V A Rodionov and V A Zhuravlev
Tomsk State University, Lenina av., 36, Tomsk, 634050 Russia

E-mail: morridin70rus@mail.ru,

Abstract. In this work, the simulations of magnetic properties of nano-sized manganese ferrite particles with zinc replacement were performed. The percentage of replacement laid in range from 0% to 80%. The parameters of particles, including exchange integrals, were taken from experimental data received for $Mn_xZn_{1-x}Fe_2O_4$. The sizes of particles and thickness of defective surface layer were taken, taking into account real sizes distribution for manganese nanoparticles received by the way of mechanochemical synthesis. Simulations were performed using the Monte-Carlo methods, Metropolis algorithm.

1. Introduction

The interest in researching of magnetic properties of nanosized ferrites arose because of the wide use of ferrites in different practical areas, such as in medical purposes, in information storage devices, in absorbing coatings and in other different areas [1, 2]. In nanosized state the properties of ferrites may significantly differ from such properties for bulk material, this difference is especially significant for such properties as the total magnetic moment of particle, Curie temperature and magnetocrystalline anisotropy [3, 4]. In this regard, for predicting the properties of synthesized materials, simulations of behavior of nanosized ferrospinels while changing external parameters such as temperature and external magnetic field or while changing the composition of the substance, including the introduction of non-magnetic impurities in the material are needed.

To date, several different models for simulations of nanosized ferrimagnetic nanoparticles were suggested [5-12]. These models study particles of different dimensions, such as a three-dimensional [5-10] and quasi-one- dimensional [11, 12], moreover, models for three-dimensional particles differs from each other by count of layers including inner volume of particle, surface layer and some quantity of intermediate layers. Most of these models have antiferromagnetic interaction in surface layer [5-9], for inner volume the type of exchange interaction for some models is ferromagnetic [5, 6, 8] and for others is antiferromagnetic [7, 9]. In studied works, the model Hamiltonians for three-dimensional models take into account exchange between near neighbors in different layers, magnetocrystalline anisotropy for surface layer and for inner volume and influence of outer magnetic field. For quasi-one-dimensional models the Hamiltonians take into account exchange interactions between neighbors up to fourth coordination sphere, also in work [12] the model takes into account the possibility of nonmagnetic replacement. All models presented above lack binding with the concrete material and values of exchange integrals and anisotropy constants aren't presented, moreover, there are no three-dimensional models which take into account the possibility of non-magnetic replacement.
In all studied works the Monte-Carlo methods [13], Metropolis algorithm [5-9, 11, 12] or kinetic algorithm [10] are used for simulations.

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In present work the three-dimensional model for nanosized manganese ferrospinel $Mn_xZn_{1-x}Fe_2O_4$ with non-magnetic replacement $0 \le x \le 0.8$ is studied. The simulations of spin configuration and specific saturation magnetization changes depending of temperature and non-magnetic replacement were performed. In the calculations we used the values of the exchange integrals given in [15] for the bulk samples of spinel $Mn_xZn_{1-x}Fe_2O_4$.

2. Description of the model and features of the algorithm

The structure of the model is represented by sphere, which is inscribed in cube with side equal to several elementary cells size, in that sphere there is another one, which represents inner volume, and difference between outer and inner spheres represents surface layer.

The peculiarity of the used model is phenomenological accounting dependency from the temperature. This model has two layers, surface layer and inner volume, but because of specifics of energy calculation there appears an implicitly defined intermediate layer, it happens because of interaction between atoms of surface layer with atoms of inner volume.

For simulation was used the Hamiltonian, which takes into account exchange interactions between near neighbors, magnetocrystalline anisotropy in surface layer and inner volume and influence of applied outer magnetic field. This Hamiltonian has the form [14]:

$$\begin{aligned} H = &-J^c_{ab} m^c_a(T) m^c_b(T) \sum_{i \neq j \in c} \vec{S}_i \vec{S}_j - J^c_{bb} (m^c_b(T))^2 \sum_{i \neq j \in c} \vec{S}_i \vec{S}_j - J^s_{ab} m^s_a(T) m^s_b(T) \sum_{i \neq j \in s} \vec{S}_i \vec{S}_j - \\ &- J^s_{bb} (m^s_b(T))^2 \sum_{i \neq j \in s} \vec{S}_i \vec{S}_j - K_c (m^c_a(T))^2 (m^c_b(T))^2 \sum_i (S^2_{ix} S^2_{iy} + S^2_{iy} S^2_{iz} + S^2_{ix} S^2_{iz}) \\ &- K_s m^s_a(T) m^s_b(T) \sum_k (S_k \vec{e}_k)^2 - g \mu_B \vec{H}_0 m(T) \sum_i \vec{S}_i, \end{aligned} \tag{1}$$

where index ***c*** is used for ions of the inner volume of the particle, index ***s*** – is used for ions of the surface layer, J^x_{ij} – value of exchange integral in the corresponding sublattice, K_c – constant of the magnetocrystalline anisotropy in inner volume of the particle, K_s – constant of the magnetocrystalline anisotropy in surface layer, H_0 – the value of applied outer magnetic field, g – g-factor, μ_B – Bohr magneton. Unit vector e_k determines the relative location of the spins in the first coordination sphere of the considered ion in the surface layer and is defined by the following formula:

$$\vec{e}_k = \sum_i (\vec{p}_k - \vec{p}_i) \Big/ \left| \sum_i (\vec{p}_k - \vec{p}_i) \right|. \tag{2}$$

Where vector p_k – unit radius-vector of the spatial orientation of the spin of selected metal ion, and vector p_i – unit radius-vector of the spin orientation for its nearest neighbors. $m_{a,b}{}^c$ and $m_{a,b}{}^s$ – normalized magnetizations of tetrahedral and octahedral sublattices internal volume and the surface layer of the particle, respectively. They are calculated by the following formula:

$$m^i_a(T) = m^i_a(0) * B\left(\frac{g\mu_b S_a H_0 + (\frac{S_a + S_b}{2})^2 z_{ab} J^i_{ab} + S^2_a z_{aa} J^i_{aa}}{kT}\right) \tag{3}$$

$$m^i_b(T) = m^i_b(0) * B\left(\frac{g\mu_b S_b H_0 + (\frac{S_a + S_b}{2})^2 z_{ba} J^i_{ab} + S^2_b z_{bb} J^i_{bb}}{kT}\right). \tag{4}$$

There $m^i_a(0)$ and $m^i_b(0)$ – magnetizations of the particle for corresponding sublattices at T = 0 K, where index i shows belonging to surface layer or to internal volume, $B(x)$ – Brillouin function, S_a and S_b – values of spins for magnetic ions of corresponding sublattices, H_0 – applied magnetic field, z_{aa}, zab, z_{ba} and z_{bb}, – the number of nearest neighbours for selected metal ions, where first index shows the type of the sublattice for selected metal ion, and second one shows the type of the sublattice for its neighbors, $J_{aa}{}^i$, $J_{ab}{}^i$ and $J_{bb}{}^i$ – exchange integrals for magnetic ions of corresponding sublattices and index i shows belonging to surface layer or to internal volume. In the formation of the arguments for the Brillouin function, the exchange interaction between atoms within the A sublattice is also taken

into account, it gives insignificant contribution to the total energy of the particle, but noticeably affect the results obtained for the normalized magnetizations.

Also, there was developed the algorithm to simulate the presence of a non-magnetic replacement, it allows to relatively uniformly replace the randomly selected manganese ions by zinc ions. This algorithm is used at the stage of the model creation after the model is formed without replacement, and is as follows:

1) Calculating the quantity of atoms in A sublattice.
2) Calculating the total quantity of atoms for replacement

$$CA_{rep} = CA * Rep. \quad (5)$$

Where CA – total quantity of atoms in A sublattice, which lay in sphere, and Rep – percentage of replacement.

3) Calculating quantity of atoms for replacement in A sublattice, which lay in sphere, for each elementary cell of the particle.
   Calculations are made the fallowing way:
   a. Calculating CA^i - the quantity of atoms in A sublattice, which lay in sphere, for each elementary cell.
   b. For each elementary cell the minimal quantity of atoms for replacement is set:

$$CA^i_{rep} = Trunk(CA^i * Rep), \quad (6)$$

   where $Trunk(x)$ – the function of discarding the fractional part.
   c. Calculating difference between total quantity of atoms for replacement and the sum obtained by the formula (6) of atoms for replacement in all cells. This difference is the quantity of the remaining atoms for replacement.
   d. Then the random set of cells is selected, the number of selected cells in this set is equal to the difference obtained in the preceding paragraph, the quantity of atoms for replacement in these cells increases by one.
4) For each cell, the quantity of atoms, obtained in the previous step, is replaced. Atoms for replacement are randomly selected and their values of the exchange integrals, anisotropy constants and the influence of the contribution of the external magnetic field are set to zero.

3. The results of modeling ferrospinels $Mn_xZn_{1-x}Fe_2O_4$

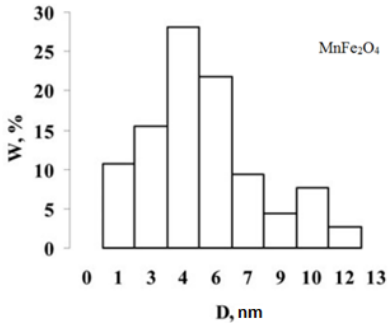

Figure 1. The distribution of nanoparticle sizes of manganese ferrite [3, 4].

Particles with size from 4 to 9 nm were selected for the simulation, that corresponds to the maximum of the size distribution for $MnFe_2O_4$ nanoparticles which was produced by mechanochemical synthesis method from salt systems [3, 4] (Figure 1).

The size range for particles from 5*a* to 9*a* , with the thickness of the surface layer 1*a*, where *a* - the size of the elementary cell of manganese ferrospinel, was selected for modeling, based on the data, presented in Figure 1. Such particles contain from 1.5 to 9 thousand magnetic ions [14].

For manganese spinel was discussed the situation with the substitution of the manganese atoms by the zinc atoms: $Mn_xZn_{1-x}Fe_2O_4$, the values of x = 0.2; 0.4; 0.6; 0.8 were considered. When substituting part of manganese atoms by zinc atoms, values of the exchange integrals differ, values exchange integrals for the internal volume for particles with different substitution percentage [15], are shown in Table 1, the exchange integrals for the surface layer are halved:

Table 1. The values of the exchange integrals for $Mn_xZn_{1-x}Fe_2O_4$ for different values of x.

Material	J_{AA}	J_{BB}	J_{AB}
$MnFe_2O_4$	-2K	-4K	-14K
$Mn_{0.8}Zn_{0.2}Fe_2O_4$	-2K	-4K	-14K
$Mn_{0.6}Zn_{0.4}Fe_2O_4$	-2K	-3.9K	-13.5K
$Mn_{0.4}Zn_{0.6}Fe_2O_4$	-2K	-3.8K	-13K
$Mn_{0.2}Zn_{0.8}Fe_2O_4$	-2.2K	-4.2K	-12.4K

For these materials were carried out calculations of the Curie temperature for quasi-bulk particles, i.e., particles without the defect surface layer. The obtained simulation results are very close to the experimental ones [15] (Figure 2.):

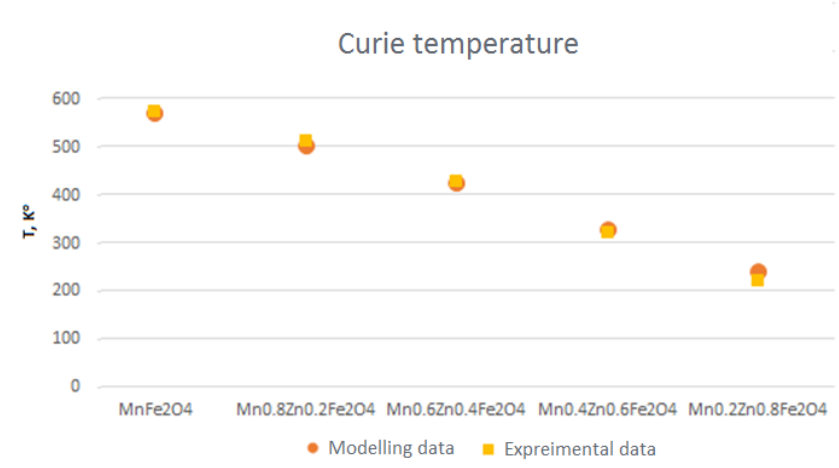

Figure 2. Dependency of Curie temperature T_c from ferrimagnetic particles composition.

Also the values of specific saturation magnetization for quasi-massive samples with different substitution values were performed (Table 2.):

Table 2. The values of specific saturation magnetization for $Mn_xZn_{1-x}Fe_2O_4$ for different values of x.

Concentration	x=1	x=0.8	x=0.6	x=0.4
Calculated	83	67	37	17
Experimental	80 [16]	69 [17]	41 [18]	23 [18]

According to the Table 2, the calculated values of the specific saturation magnetization are close to the experimental data [16-18].

The simulation results of change of the spin configuration when temperature changes for nanosized particles of manganese-zinc ferrospinel, show that the addition of nonmagnetic impurities significantly affects the speed of the particles transition to the paramagnetic state when heated. From Figure 3, which shows the dependence for $Mn_{0.8}Zn_{0.2}Fe_2O_4$ and $Mn_{0.6}Zn_{0.4}Fe_2O_4$, and figure 4, which shows the dependence of $Mn_{0.4}Zn_{0.6}Fe_2O_4$, is clear that with increasing percentage of atoms, which were replaced by non-magnetic ones, the Curie temperature decreases significantly. Graphics also reflect the fact that reducing the particle size in the case of nonmagnetic replacement in the nanoparticle of ferrospinel, similarly to the case without the replacement, results in a reduction of the specific magnetization of substitution and more rapid transition to the paramagnetic state. The bursts of magnetization, which are present on the graphs, are caused by a full transition of the surface layer in the paramagnetic state, at given temperatures, that may cause random ordering for surface atoms, which affect the atoms of inner layer, that is more important for the particles with small size.

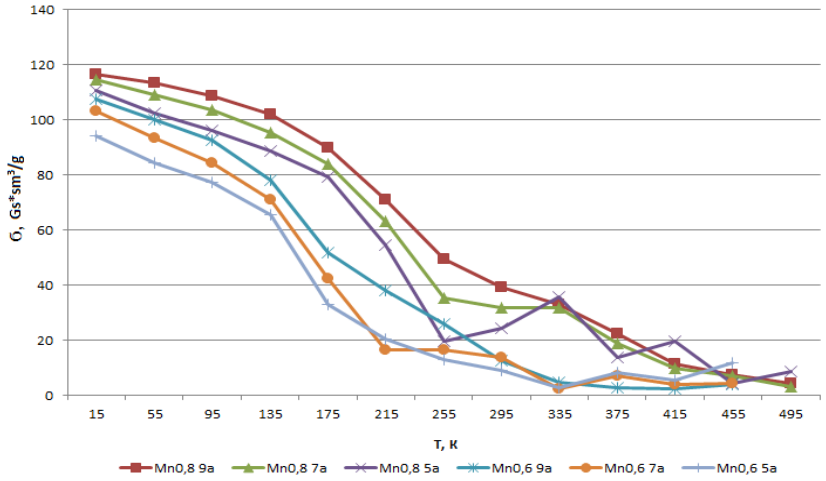

Figure 3. The temperature dependence of the specific saturation magnetization, for $Mn_{0.8}Zn_{0.2}Fe_2O_4$ and $Mn_{0.6}Zn_{0.4}Fe_2O_4$ particles, with sizes 5, 7 and 9 elementary cells.

By increasing the percentage of nonmagnetic replacement of up to 60%, for the nanosized particles, the transition to the paramagnetic state occurs before the reaching the room temperature (Figure 4.), which distinguishes this case from massive material, which has the Curie temperature of 315 K [15].

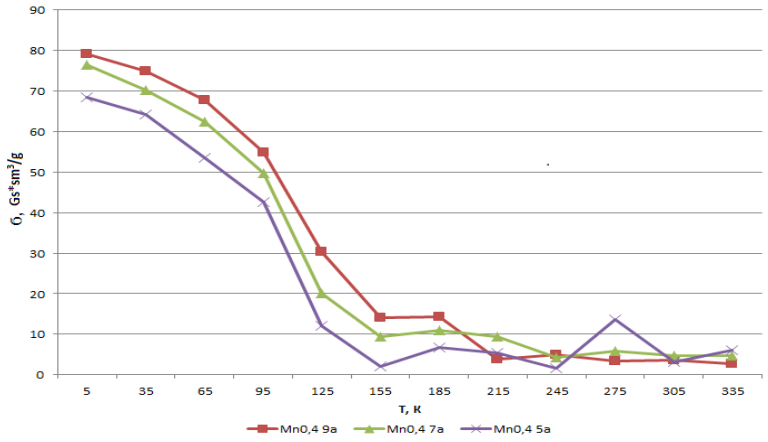

Figure 4. The temperature dependence of the specific saturation magnetization, for $Mn_{0.4}Zn_{0.6}Fe_2O_4$ particles with sizes 5, 7 and 9 elementary cells.

4. Conclusion

The paper described a technique for modeling spin configuration of nanoscale ferrimagnets with a spinel structure, and the results of the modeling of manganese ferrospinel, with the replacement of manganese ions by nonmagnetic ions of zinc in varying proportions were given. The simulation results showed that by increasing the proportion of non-magnetic replacement, the Curie temperature of both the bulk material and nanoparticles for manganese ferrite spinel significantly decreases, thus, transition to the paramagnetic state for nanoparticles is much faster due to the influence of the surface layer, nanoparticles with smaller size have a lower Curie temperature. Thus, to nanoparticles of manganese ferrospinel with nonmagnetic substitution of 60%, the Curie temperature falls below room temperature, while for the bulk samples it lies in the range above room temperature.

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