Physical properties of FePt nanocomposite doped with Ag atoms: First-principles study*

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(Received 4 September 2013; revised manuscript received 13 December 2013; published online 22 May 2014)

$L1_0$ FePt nanocomposite with high magnetocrystalline anisotropy energy has been extensively investigated in the fields of ultra-high density magnetic recording media. However, the order–disorder transition temperature of the nanocomposite is higher than 600 °C, which is a disadvantage for the use of the material due to the sustained growth of FePt grain under the temperature. To address the problem, addition of Ag atoms has been proposed, but the magnetic properties of the doped system are still unclear so far. Here in this paper, we use first-principles method to study the lattice parameters, formation energy, electronic structure, atomic magnetic moment and order–disorder transition temperature of $L1_0$ FePt with Ag atom doping. The results show that the formation energy of a Ag atom substituting for a Pt site is 1.309 eV, which is lower than that of substituting for an Fe site 1.346 eV. The formation energy of substituting for the two nearest Pt sites is 2.560 eV lower than that of substituting for the further sites 2.621 eV, which indicates that Ag dopants tend to segregate $L1_0$ FePt. The special quasirandom structures (SQSs) for the pure FePt and the FePt doped with two Ag atoms at the stable Pt sites show that the order–disorder transition temperatures are 1377 °C and 600 °C, respectively, suggesting that the transition temperature can be reduced with Ag atom, and therefore the FePt grain growth is suppressed. The saturation magnetizations of the pure FePt and the two Ag atoms doped FePt are 1083 emu/cc and 1062 emu/cc, respectively, indicating that the magnetic property of the doped system is almost unchanged.

Keywords: FePt, Ag, density functional theory (DFT), order–disorder transition

PACS: 61.66.Dk, 71.15.Mb, 64.60.Cn **DOI:** 10.1088/1674-1056/23/7/076105

1. Introduction

As is well known that the order $L1_0$ FePt nanocomposite films have attracted much attention as perpendicular magnetic recording media, owing to high coercivity H_c and very high magnetocrystalline anisotropy energy ($K_u \sim 7\times10^7$ erg/cm^3).[1–7] However, the deposited FePt films need a high annealing temperature of over 600 °C to transform the disordered face-centered-cubic phase into ordered face-centered-tetragonal $L1_0$ FePt phase.[8–13] The disadvantage is that the annealing temperature can cause the sustained growth of the grains, which seriously reduces the magnetic recording density of the FePt film. Researchers have proposed that the addition of Ag atom can reduce the ordering temperature.[14–20] The standpoint is that immiscible Ag atoms added to FePt thin film can change the film structure from an interconnected network to a completely isolated island structure. Therefore, the growth of the grains can be suppressed and the signal-to-noise ratio of the thin-film material is increased.[21–23] Although the experiments have been carried out currently to examine the performance of the FePt system, it is very necessary to investigate the magnetic properties by a sophisticated theoretical method.

In this article, we calculate the lattice parameters, formation energy, electronic structure, atomic magnetic moment, and order–disorder transition temperature of $L1_0$ FePt doped with a Ag atom using the first-principles method. The results show that the transition temperature can be reduced, therefore suppressing the FePt grain growth. While the main magnetic properties of the doped system remain unchanged.

2. Computational methods

The calculations are based on the density functional theory using the Vienna *ab initio* simulation package (VASP) code.[24] The electron–electron interaction is represented by a projector augmented wave (PAW) approach using the generalized gradient approximation (GGA) of Perdew. The cutoff energy of 435.4 eV is used for the plane-wave basis set. The Brillouin zone is sampled by using Monkhorst and Pack's k-points of a $5\times5\times5$ grid for all structure calculations. The convergence criteria for structure optimization and energy calculation are set to be an energy tolerance of 1.0×10^{-4} eV/atom and a maximum force tolerance of 1.0×10^{-3} eV/Å, respectively. When the energy tolerance and the maximum force tolerance are set smaller to be 1.0×10^{-5} eV/atom and 1.0×10^{-4} eV/Å, respectively, the percent changes of the ground state energies are less than 0.001%, and the percentage changes of physical

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11274033 and 61227902) and the Research Fund for the Doctoral Program of Higher Education of China (Grant No. 20131102130005).

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quantities are less than 0.1%, so the results obtained under the smaller energy tolerance and the smaller maximum force tolerance are consistent with the current results.

$L1_0$ FePt nanocomposite has a face-centered-tetragonal structure. Single atomic layers of Fe and Pt alternate along the c axis. A 2×2×2 supercell (Fig. 1) including 16 Fe and 16 Pt atoms is selected to calculate the structures of the pure $L1_0$ FePt, $L1_0$ FePt doped with one Ag atom, and $L1_0$ FePt doped with two Ag atoms. Then the corresponding 32-atom special quasirandom structures (SQSs) (see Ref. [25] for atomic coordinates) are also calculated. The atomic coordinates of Ag atoms substituting for the atoms in $L1_0$ and SQSs FePt are listed in Table 1. The $L1_0$ FePt doped with one Ag atom uses the model of Pt in the center site, and the others use the model of Fe in the center site. In all the calculations of SQSs, the unified atomic coordinates are used. The cells for relaxation are first calculated, and then the relaxed cells are statically calculated to obtain the final energy, charge density, density of state, etc.

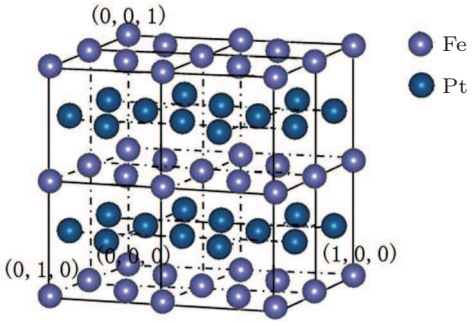


Fig. 1. (color online) 2×2×2 $L1_0$ FePt supercell structure with $x_{Fe} = 0.5$ and $x_{Pt} = 0.5$.

Table 1. Ag substituted atom coordinates. The lattice parameter of the unit cell is $a = 0.375$ nm.

FePt structure	Lattice vectors	Substituted atoms	Atom coordinates
$L1_0$	$a_x = [2,0,0]a$ $a_y = [0,2,0]a$ $a_z = [0,0,2]a$	1Fe	(0.5, 0.5, 0.5)
		1Pt	(0.5, 0.5, 0.5)
		2Fe(nearest)	(0.5, 0.25, 0) (0.75, 0.25, 0.5)
		2Fe (far)	(0.5, 0.5, 0.5) (0.0, 0.0, 0.0)
		2 Pt (nearest)	(0.25, 0, 0.25) (0.5, 0.25, 0.25)
		2Pt (far)	(0.25, 0.5, 0.25) (0.75, 0, 0.75)
		1Fe1Pt (nearest)	(0.5, 0.5, 0.5) (0.25, 0.5, 0.25)
		1Fe1Pt (far)	(0.5, 0.5, 0.5) (0.25, 0.0, 0.75)
SQS	$a_x = [-0.5,-0.5,1]a$ $a_y = [-1.5,-1,-1.5]a$ $a_z = [2,-2,0]a$	1Fe	(2/8, 2/4, 14/32)
		1Pt	(3/8, 1/4, 9/32)
		2Fe	(4/8, 0.0, 20/32) (4/8, 0.0, 28/32)
		2Pt	(3/8, 1/4, 9/32) (3/8, 1/4, 17/32)

The formation energy E_f of Ag atoms substituting for the atoms in the $L1_0$ FePt is obtained from the following calculation formula:

$$E_f = E_{FePt\cdot Ag} - E_{FePt} - nE_{Ag} + mE_{Fe} + (n-m)E_{Pt}, \quad (1)$$

where $E_{FePt\cdot Ag}$ denotes the total energy of $L1_0$ FePt doped with Ag atoms; E_{FePt} denotes the total energy of pure $L1_0$ FePt; E_{Ag}, E_{Fe}, and E_{Pt} represent the elemental alloy energies of Ag, Fe, and Pt; n and m refer to the numbers of added Ag atoms and substituted Fe atoms.

The saturation magnetizations, M_S , of pure $L1_0$ FePt and $L1_0$ FePt doped with Ag atoms are obtained from the following formula:

$$M_S = m/V. \quad (2)$$

Herein, m is the total magnetic moment in units of Bohr magneton μ_B, and V denotes the cell volume. The value of μ_B is given by

$$\mu_B = eh/(4\pi m_e), \quad (3)$$

where e is the electron charge, h represents the Planck constant, and m_e denotes the electron mass.

The SQSs proposed by Zunger *et al.* are employed in the calculation of transition temperature.[26] The SQS is a random disordered structure model, and is specially designed for small-unit-cell periodic structures with only a few atoms per unit cell. The first-principles DFT calculation of SQSs can obtain some important physical quantities of disorder nanocomposite, such as the formation enthalpy. Then we can obtain a crude estimate of the FePt order–disorder transition temperature using the following equation:[27]

$$T_C \approx (\Delta H^{SQS} - \Delta H^{L1_0})/\Delta S_{ideal}, \quad (4)$$

where ΔH^{SQS} and ΔH^{L1_0} are the formation enthalpies of SQS and $L1_0$ FePt, respectively. An ideal configurational entropy is $\Delta S_{ideal} = -R(x_{Fe}\ln(x_{Fe}) + x_{Pt}\ln(x_{Pt}) + x_{Ag}\ln(x_{Ag}))$, in which R is the molar gas constant, equal to 8.31 J/(mol·K).

3. Results and discussion

3.1. Crystal structure

The relaxed lattice parameters are shown in Table 2. The relaxed lattice constants of pure $L1_0$ FePt are $a = 0.3869$ nm and $c = 0.3769$ nm, and the c/a ratio is 0.974. The lattice parameter and c/a ratio are in good agreement with the experimental values ($a = 0.386 \pm 0.01$ nm, $c = 0.371 \pm 0.01$ nm, $c/a = 0.961 \pm 0.03$;[28] $a = 0.3857$ nm, $c = 0.3719$ nm, $c/a = 0.964$[29]). From these data, we can see that a comparison of lattice parameters between pure $L1_0$ FePt and a Ag atom substituting for an Fe site shows that the pure $L1_0$ FePt has a greater change than a Ag atom substituting for a Pt site, and the changes in lattice parameters of two Ag atoms substituting for the nearest atoms are smaller than those caused by two Ag atoms substituting for far atoms.

The results of the formation energies are shown in Table 3. It shows that the formation energy of a Ag atom substituting for a Pt atom is lower than that of a Ag atom substituting for an Fe atom, and all the formation energies of two Ag atoms substituting the nearest atoms are lower than those of two Ag atoms substituting the far atoms. Hence, the results indicate that the Ag dopants prefer to substitute Pt sites and tend to segregate from $L1_0$ FePt. This agrees well with the analysis of lattice constants.

Table 2. Relaxed lattice parameters of FePt.

Ag substitution	a/nm	b/nm	c/nm	c/a	$\Delta a/a$	$\Delta c/c$	$\Delta(c/a)$
Pure	0.3869	0.3869	0.3769	0.974	–	–	–
1Fe	0.3889	0.3889	0.3779	0.971	0.517%	0.265%	0.003
1Pt	0.3874	0.3874	0.3774	0.974	0.129%	0.132%	0
2Fe(nearest)	0.3902	0.3902	0.3790	0.971	0.853%	0.557%	0.003
2Fe(far)	0.3906	0.3906	0.3800	0.973	0.956%	0.822%	0.001
2Pt(nearest)	0.3876	0.3876	0.3784	0.976	0.180%	0.398%	0.002
2Pt(far)	0.3878	0.3878	0.3781	0.975	0.232%	0.318%	0.001
1Fe1Pt(nearest)	0.3892	0.3898	0.3783	0.972	0.594%	0.371%	0.002
1Fe1Pt(far)	0.3926	0.3927	0.3821	0.973	1.473%	1.380%	0.001

Table 3. Formation energies of Ag atoms on the Fe site and/or the Pt site.

Ag substitution	1Fe	1Pt	2Fe (nearest)	2Fe (far)	2Pt (nearest)	2Pt (far)	1Fe1Pt (nearest)	1Fe1Pt (far)
E_f/eV	1.346	1.309	2.600	2.682	2.560	2.621	2.541	2.919

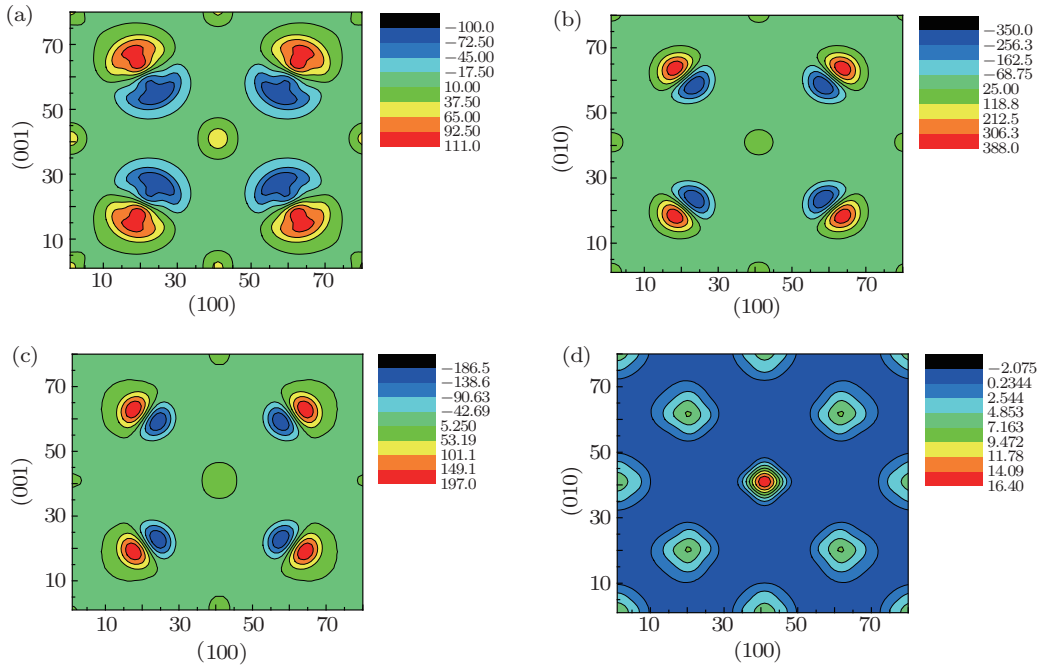


Fig. 2. (color online) Differential charge densities between relaxation and non-relaxation for (a) (010) face Ag atom substituting for Fe atom, (b) (001) face Ag atom substituting for Fe atom, (c) (010) face Ag atom substituting for Pt atom, and (d) (001) face Ag atom substituting for Pt atom.

Through investigating the charge density distribution, we can know more about the Ag dopants affecting the electrons distribution and bond making. Figure 2 shows the differential charge densities between relaxation and non-relaxation of a Ag atom substituting an Fe atom in the Fe center model or a Ag atom substituting for a Pt in the Pt center model. It can be seen that the doped Ag atoms can make the charges move out, and the changed charge density distribution of Ag atoms substituting for Fe atoms is larger than that of Ag atoms substituting for Pt atoms. This is consistent with the above conclusion from the lattice parameters and formation energy analysis.

3.2. Magnetic property

The values of saturation magnetization M_S are shown in Table 4. The calculated results show that the saturation magnetization of pure $L1_0$ FePt is 1083 emu/cc, which is in close agreement with the available experimental values (1125 ± 60 emu/cc,[30] 1100 ± 50 emu/cc[31]) The saturation magnetization of $L1_0$ FePt doped with Ag atoms substituting for Pt sites has smaller changes than that of Ag atoms substituting for Fe sites. This is because the magnetism of $L1_0$ FePt mainly derives from the contribution of magnetic Fe atoms, and both Pt and Ag atoms are the non-magnetic atoms. Comparing all the data, we can see that the addition of Ag atoms has less influence on the saturation magnetization of $L1_0$ FePt. Figure 3 shows the densities of state (DOSs) of spin-up and spin-down states, showing that the magnetism is mainly attributed to the contribution of the magnetic moment of net spin down electrons above the Fermi face.

Table 4. Saturation magnetization, M_S, of FePt.

Ag substitution	Pure	1Fe	1Pt	2Fe (nearest)	2Fe (far)	2Pt (nearest)	2Pt (far)	1Fe1Pt (nearest)	1Fe1Pt (far)
m/μ_B	52.73	50.13	52.46	47.13	47.52	52.06	52.17	49.97	50.69
V/Å^3	451.3	457.2	453.0	461.7	463.7	454.6	454.8	458.8	471.2
M_S/emu·cc^{-1}	1083	1017	1074	947	950	1062	1064	1010	998

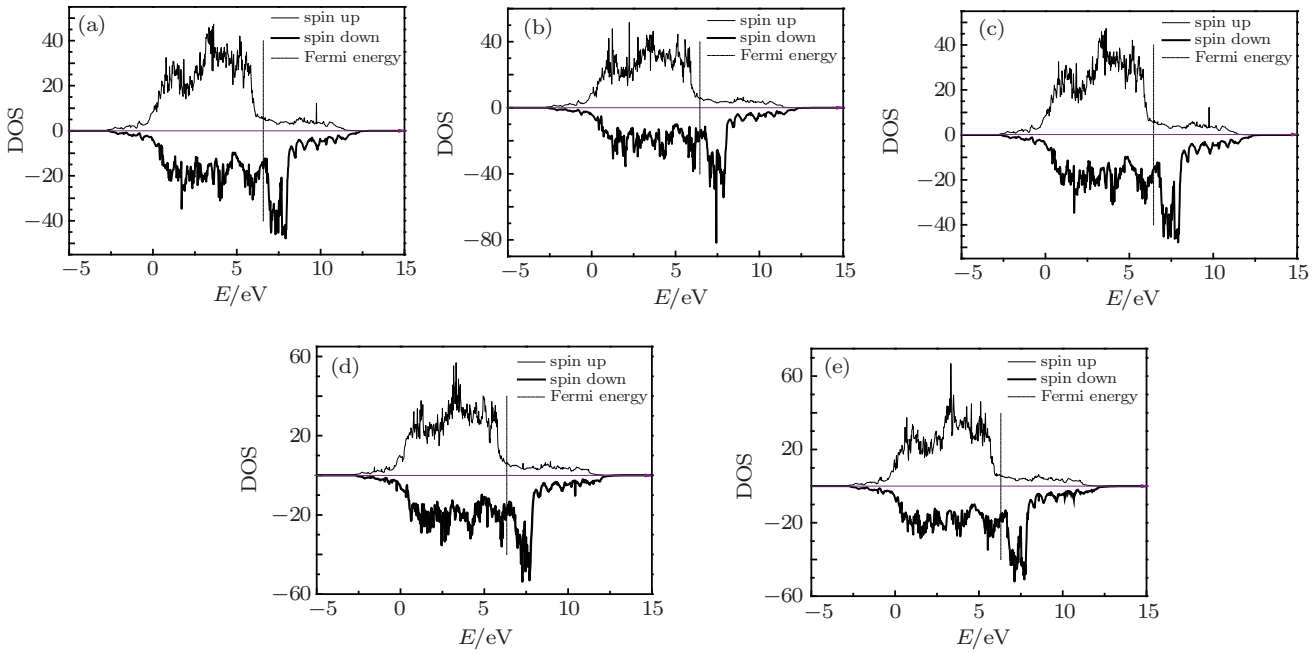


Fig. 3. DOSs of spin-up and spin-down states for (a) pure $L1_0$ FePt, (b) one Ag atom substituting for Fe atom, (c) one Ag atom substituting for Pt atom, (d) two Ag atoms substituting for the nearest Fe atoms, and (e) two Ag atoms substituting for the nearest Pt atoms.

3.3. Order–disorder transition temperature

The calculated order–disorder transition temperature of $L1_0$ FePt is 1650 K. It is about 100 K higher than the experimental transition temperature value (about 1573 K), and the calculated value (1530 K from the Monte Carlo stimulations).[32] The order–disorder transition temperature of FePt doped with one Ag atom substituting for an Fe or a Pt site, and that of FePt doped with two Ag atoms substituting for the Fe or Pt sites are 1251 K or 1159 K, and 988 K or 873 K, respectively. Thus, it can be seen that the order–disorder transition temperature is effectively reduced when Ag atoms are added to FePt nanocomposite, and the order–disorder transition temperature decreases with the increase in Ag dopants.

4. Conclusion

A first-principles method using projector augmented-wave (PAW) based on density functional theory is used to calculate the equilibrium geometry, formation energy, electronic structure, and atomic magnetic moment of FePt nanocomposite doped with Ag atoms in the dilute concentration.

The changed energy of one Ag atom substituting for an Fe site is 1.346 eV, while that of one Ag atom substituting for a Pt site is 1.309 eV. Meanwhile, the charge density and lattice constant of one Ag atom substituting for an Fe site have a greater change than those of one Ag atom substituting for a Pt site. Therefore, Ag dopants prefer to occupy the substitutional sites of Pt in $L1_0$ FePt. The changed energy of Ag atom substituting for the nearest sites is lower than for the far neighbors, so Ag dopants tend to segregate $L1_0$ FePt.

The saturation magnetizations of the pure $L1_0$ FePt, $L1_0$ FePt doped with two Ag atoms substituting for Pt sites are 1083 and 1062 emu/cc, respectively. The magnetic properties of FePt nanocomposite doped with Ag atoms are also well compared with those of pure FePt nanocomposite.

The order–disorder transition temperatures of $L1_0$ FePt doped and $L1_0$ FePt doped with two Ag atoms substituting for Pt sites are 1650 K and 873 K, respectively. Therefore, doping Ag into the FePt bulk nanocomposite is an efficient way to reduce the order–disorder transition temperature, and all the results are in good agreement with other calculated and experimental results.

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