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AB INITIO CALCULATION OF VACANCY FORMATION ENERGY IN ANTIPEROVSKITE Mn_3GaC

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In this article, we presented the ab initio calculation of vacancy formation energy according to Schottky in the alloy Mn_3GaC. Calculations were carried out in the frameworks of the density functional theory (DFT), implemented in VASP software package. For approximation of the exchange-correlation functional, the generalized gradient approximation in the Perdew–Burke–Ernzerhof formulation was used. It was shown that for the alloy under research, the most energetically favorable formation of a vacancy is in the place of C atom; formation of vacancies in places of Mn atoms is also beneficial, whereas the Ga vacancies are energetically unfavorable. Also, the concentration of vacancies at a finite temperature was calculated. It was shown that Mn and C vacancies have almost identical equilibrium concentration at a nonzero temperature; at that, the concentration of Ga vacancies is negligibly small. In addition, elastic moduli for various magnetic orderings (ferromagnetic, noncollinear, and antiferromagnetic) in the alloy under research were calculated. Using the quasi-harmonic Debye model, the Helmholtz free energy curves were constructed. Using these curves, it was also shown that Schottky monovacancies do not destabilize the ferromagnetic phase. Stability of the ferromagnetic phase is due to the large contribution of magnetic entropy to the Helmholtz free energy for the alloy under research.

Keywords: vacancy; vacancy formation energy; Helmholtz free energy; ab initio.

1. Introduction

The ternary X_3YC carbide phases formed with the participation of d-metals VIIa-, VIIIa- subgroups (X) and non-transition elements IIb–VIb-subgroups (Y) have a simple cubic structure of antiperovskitetype [1]. Being in the high-temperature region of paramagnets of the type, a series of perovskite-like carbides undergoes tetragonal lattice distortions at low temperature s and exhibits magnetic properties that correspond to the formation of several possible types of magnetic structures.

Antiperovskite compounds of the Mn_3GaC type are interesting due to their relatively simple and stable cubic structure, numerous possible technological applications (sensors, microelectromechanical systems, storage devices, etc.) [2–6] and a wide range of properties such as: the giant magnetoresistance, magnetovolume effect, giant negative thermal expansion, magnetostriction. Moreover, this type of compounds can be used as a refrigerant for magnetic cooling devices [7], thanks to the presence of its magnetocaloric effect, which is observed around the magnetic phase transitions [8–12].

2. Computational details

The total energy of the studied alloy was calculated using the density functional theory implemented in the VASP [12, 13]. For approximation of exchange correlation potential was used the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) formulation [13]. For VASP pseudopotentials we used the follow electronic configurations: $Mn(3p^6 3d^6 4s^1)$, $C(1s^1 2s^2 2p^2)$, $Ga(4d^{10} 4s^2 4p^1)$. The kinetic energy cut-off was taken to be 500 eV. A Monkhorst-Pack grid was employed to sample the Brillouin zone [14]. Grid *k*-points 8×8×8 was used.

In this paper, a defect of the vacancy type was considered. Calculations of the energy of the crystal containing the vacancy were performed on 90 atomic supercells. The super cell was obtained from the unit cell by means of translations (3 3 2). In this supercell, an atom (Mn, Ga or C) was removed near the center.

The defect formation energy is calculated with the following equations:

$$E_V = E_{def} - E_0 + n_{\mathrm{Mn}}\mu^0_{\mathrm{Mn}} + n_{\mathrm{Ga}}\mu^0_{\mathrm{Ga}} + n_{\mathrm{C}}\mu^0_{\mathrm{C}}. \quad (1)$$

E_V is the energy of the crystal containing the defect, E_0 is the energy of an ideal crystal, n_i is defect concentration for Mn, Ga, C, respectively, μ is chemical potential of an isolated atom. In order to study thermodynamical properties of materials studied under finite temperature and pressure, we applied the quasi-harmonic Debye model. Free energy was calculated using the equation:

$$F = E + F_{vib} - TS_{mix} - TS_{mag}, \quad (2)$$

where E is the total energy of the crystal, obtained by first-principle calculations, S_{mix} is mixing entropy, S_{mag} is magnetic entropy, F_{vib} is free energy of a crystal lattice. In this work we neglect the electronic contribution to free energy, due to its smallness. Magnetic and defect formation entropy was calculated by following equation:

$$S_{mix} = k_B C_v \ln(C_v) + k_B (1 - C_v)\ln(1 - C_v); \quad (3)$$

$$S_{mag} = k_B \ln(m + 1), \quad (4)$$

where m is the magnetic moment obtained in self-consistent calculations, k_B is Boltzmann constant, C_v is concentration of vacancy. Free energy of a crystal lattice includes zero-point energy and temperature dependent part according to:

$$F_{vib} = k_B T\left(\frac{9}{8}\frac{\Theta_D}{T} + 3\ln\left(1 - e^{-\frac{\Theta_D}{T}} + D(T)\right)\right), \quad (5)$$

where Θ_D is Debye temperature, $D(T)$ is Debye function:

$$D\left(\frac{T}{\Theta_D}\right) = 3\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{x^3}{e^x - 1} dx. \quad (6)$$

In order to calculate the Debye temperature, we used the quasi-harmonic Debye model [15], where the Debye temperature can be expressed as

$$\Theta_D = \frac{h}{2\pi k_B}\sqrt[3]{6\pi^2\sqrt{V_0}\,n}\, f(\sigma)\sqrt{\frac{B}{M}}, \quad (7)$$

where k_B is the Boltzmann constant, V_0 is the equilibrium volume, n is the number of atoms per unit cell, B is the bulk modulus, M is the molar mass of compound. The function $f(\sigma)$ is given by

$$f(\sigma) = 3\left[2\left(\frac{2(1+\sigma)}{3-2\sigma}\right)^{3/2} + \left(\frac{1+\sigma}{3(1-\sigma)}\right)^{3/2}\right]^{-1}, \quad (8)$$

where σ is the Poisson's ratio.

3. Results and discussions

3.1. Properties of Mn_3GaC without defect

First, using ionic relaxation, we found the equilibrium lattice parameter, energy, and magnetic moment for various magnetic configurations shown in Fig. 1.

Table 1 shows the optimized lattice parameters, magnetic moments, and total energy for various magnetic states. For Mn_3GaC, the optimized lattice constant is found to be ≈ 3,824 Å for favorable state and ≈ 3,862 Å for noncolinear state that is slightly less than the experimental one by 1,5 % and 0,5 % respectively (≈ 3,88 Å [3, 7, 8]).

Table1

Equilibrium energy per atom, magnetic moment per unit cell, and lattice parameter for Mn_3GaC

Magnetic configuration	Total energy, eV	Magnetic moment, μ_B	Equilibrium lattice parameter, Å
FM	–7,971	4,711	3,824
NC	–7,959	0,020	3,862
AFM	–7,947	0,000	3,803

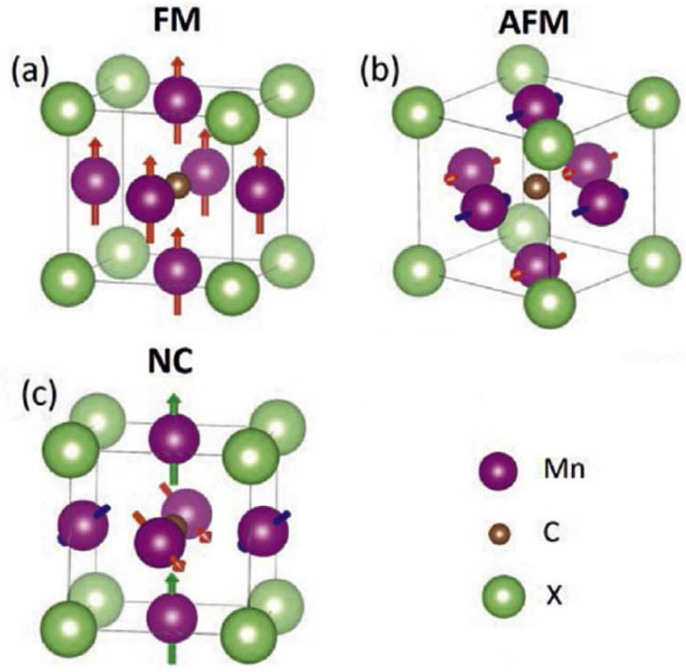

Fig. 1. Various spin configurations of Mn atoms were considered in the calculations: (a)FM, (b)AFM, (c)NC

Also, Poisson's coefficients, bulk elastic moduli and Debye temperatures, indicated in Table 2, was calculated for various magnetic orderings.

Table 2

Poisson's ratio, Young's modulus, and Debye temperature for various magnetic states

Magnetic configuration	v	E, GPa	Θ_D, K
FM	0,242	266,0	570,2
NC	0,284	179,5	465,3
AFM	0,277	286,6	584,4

3.2. Defect formation energy

The purpose of calculating the defect formation energy is to estimate the stability of the different kinds of vacancy in the parent phase in Mn_3GaC alloys.

The formation energy of a vacancy was estimated according to equation 1and it is given in Table 3. It can be seen from this table the most likely formation of a vacancy in the position of the atom C. It is also likely the formation of a vacancy Mn atoms.

Table 3

The energy of the formation of a vacancy at the site of the atom Mn, Ga and C, respectively

	Mn	Ga	C
E_v, eV	0,625	0,692	0,604

Fig. 2 shows the temperature dependence of the concentration of vacancies per cell, this concentration was estimated using the equation:

$$C_v = Ne^{-\frac{E_v}{k_B T}}, \quad (9)$$

where N is number of atoms in a cell.

As can be seen from this figure, vacancies make a visible contribution to free energy starting at a temperature of 400 K. It can also be seen that Ga vacancies are formed significantly less than vacancies at C and Mn sites. Vacancies Mn and C make about the same contribution to the entropy of mixing.

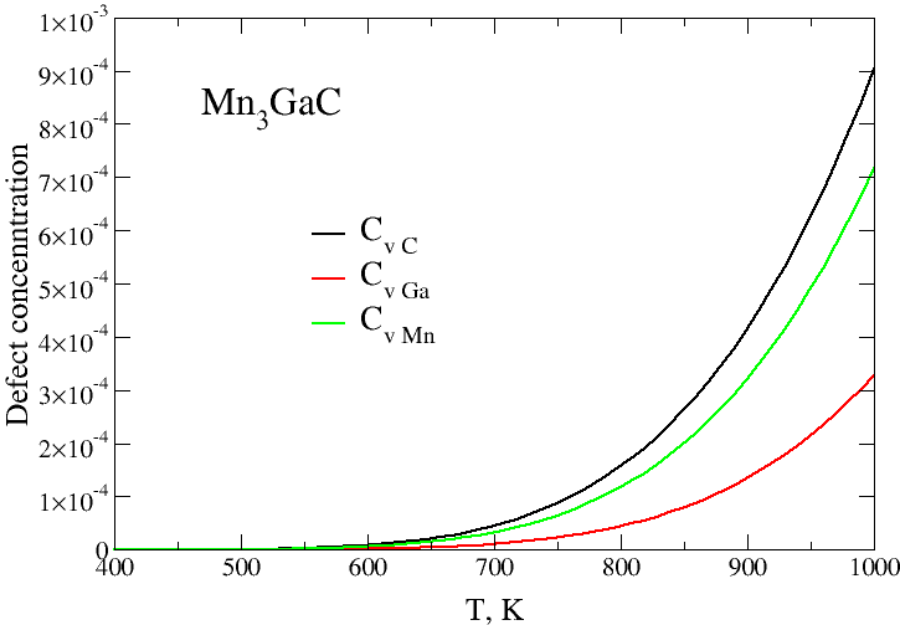

Fig. 2. Concentration of various types of vacancies in Mn_3GaC

3.3. Helmholtz free energy

To assess the stability of the various phases, the free energy of the compound under study was calculated. Figure 3 shows the dependence of the Helmholtz energy per atom versus temperature for various magnetic configurations. This graph demonstrates that monovacancies do not destabilize the FM phase in the temperature range under study. It is shown that the ferromagnetic configuration is advantageous in comparison with the antiferromagnetic and non-collinear configuration.

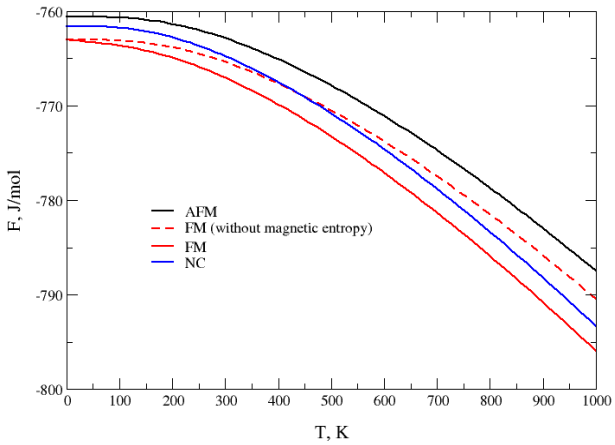

Fig. 3. Free energy for various magnetic configurations Mn_3GaC

4. Summary

Thermodynamic structural and magnetic properties were calculated for Mn_3GaC alloy within the density functional theory. Equilibrium lattice parameters, the magnetic moments, the Debye temperature, and the elastic constants are calculated for various magnetic orderings investigated alloy.

It is also shown that Schottky monovacancies do not destabilize the ferromagnetic phase. The stability of the ferromagnetic phase is due to the large contribution of magnetic entropy to free energy.

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ПЕРВОПРИНЦИПНОЕ ВЫЧИСЛЕНИЕ ЭНЕРГИИ ФОРМИРОВАНИЯ ВАКАНСИЙ В АНТИПЕРОВСКИТЕ Mn_3GaC

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В данной работе представлено первопринципное вычисление энергии образования вакансий по Шотки в сплаве Mn_3GaC. Вычисления проводились в рамках теории функционала плотности (DFT), реализованной в программном пакете VASP. Для аппроксимации обменно-корреляционного функционала использовалась обобщенная градиентная аппроксимация в формулировке Пердью–Бурке–Эйзенхофа. Показано, что в исследуемом сплаве наиболее энергетически выгодно образование вакансии на месте атома C, так же выгодно образование вакансий на местах атомов Mn, в то время как вакансии Ga являются энергетически невыгодными. Также вычислена концентрация вакансий при конечной температуре. Продемонстрировано, что вакансии Mn и C имеют практически одинаковую равновесную концентрацию при ненулевой температуре, при этом концентрация вакансий Ga пренебрежимо мала. Кроме того, рассчитаны модули упругости для различных магнитных упорядочений (ферромагнитное, неколлинеарное и антиферромагнитное) в исследуемом сплаве. Используя квазигармоническую модель Дебая, построены кривые свободной энергии Гельмгольца. Используя эти кривые, показано также, что моновакансии Шотки не дестабилизируют ферромагнитную фазу. Стабильность ферромагнитной фазы обусловлена наличием большого вклада магнитной энтропии в свободную энергию Гельмгольца для исследуемого сплава.

Ключевые слова: вакансия; энергия образования вакансий; энергия Гельмгольца; ab initio.

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