DOI: 10.14529/mmph200206

STRUCTURAL AND ELASTIC PROPERTIES OF FE-GE ALLOYS: *AB INITIO* STUDIES

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In this paper, with the help of the density functional theory, the structural and elastic properties of A2, B2, $D0_3$, and $L1_2$ phases of $Fe_{100-x}Ge_x$ alloys ($12{,}5 \le x \le 28{,}125$ at. %) have been studied. The electronic and full ionic relaxations were used for the investigation of crystal structures. The concentration dependencies of the atomic volumes, structural phase transition temperatures, tetragonal and rhombohedral shear moduli have been calculated. We show that the atomic volume curves correlate with the sequence of phase transitions observed experimentally: A2→B2→$D0_3$ ($x \le 22$ at. % of Ge content). The structural phase transition temperatures increase with the Ge concentration. The calculated tetragonal moduli for the $D0_3$, A2, and $L1_2$ structures decrease with the increasing of the Ge content, what agrees with the experimental results. The dependence of rhombohedral shear moduli as a function of Ge concentration does not change significantly with increasing Ge atoms. The C_{44} is increased for the $D0_3$ phase, while for A2, B2, and $L1_2$, it decreases.

Keywords: ab initio; crystal structure; phase transformations; elastic moduli.

Introduction

The discovery of large magnetostrictive strains in iron-gallium alloys in 1999 started the extensive study of rare-earth-free binary alloys based on α-Fe [1, 2]. These alloys are promising materials for sensors and actuator applications. Among them, iron-gallium alloys are the most thoroughly investigated. The phase diagram of Fe-Ge alloys is very similar to Fe-Ga systems in the Fe-rich region [3]. Ga and Ge are *p*-elements that have a significant influence on electronic structures of binary compounds, which, in turn, determines their structural and magnetic properties. In both alloys, in the range of Ga(Ge) content up to 12 at. %, the phase diagram is characterized by the existence of the disordered α-phase (A2 structure). At these compositions, the values of magnetostriction (λ_{100}) for Fe-Ga and Fe-Ge are similar and positive [1]. The further increase of Ga content up to 19 at. % leads to the formation of mixing phase $D0_3$+A2 [4]. The magnetostriction of $Fe_{81}Ga_{19}$ reaches $340 \cdot 10^{-6}$ in slowly cooled samples. In the case of $Fe_{81.5}Ge_{18.5}$, B2 and $D0_3$ phases are observed [6], and $\lambda_{100} = -96 \cdot 10^{-6}$ [1]. In contrast to Fe-Ga alloys, the properties of Fe-Ge systems are not well investigated. Experimental studies of phase formation and transitions in alloys with Ge additives are presented in [5–13, etc.]. For Fe-Ge alloys in the phase region $x \le 22$ at. %, three types of the base-centered cubic (*bcc*) structures with different ordering (fully disordered A2, partially ordered B2, and ordered $D0_3$) exist [5, 7, 9, 10, 13]. In the concentration range of Ge content $22 \le x \le 28$ at. %, low temperature face-centered cubic (*fcc*) $L1_2$ and high-temperature hexagonal $D0_{19}$ phases were also observed [5, 6, 8, 10–12]. The effect of the addition of Ge atoms on the elastic properties of Fe-Ge alloys is considered in [1, 14]: with the increase of Ge atoms in Fe lattice the tetragonal elastic modulus decreases.

The magnetic moments and Curie temperatures of $Fe_{100-x}Ge_x$ alloys were investigated theoretically in [15–18]. With adding of Ge atoms the total magnetic moment and Curie temperature reduced. Cao *et al*. [19] with the help of a full-potential-linearized augmented plane wave method studied the magnetostriction as a function of Ge concentration. They found that λ_{100} increased linearly with x up to 11 at. % and then decreased. In our recent work [15, 18] based on the total energy calculation of $Fe_{100-x}Ge_x$ alloys with different structures, the phase diagram as a function of x was constructed. Nevertheless, the existing theoretical results are insufficient to understand the relation between phase transformations and magneto-elastic properties.

Therefore, this study aims to investigate the structural and elastic properties of cubic phases of $Fe_{100-x}Ge_x$ ($12{,}5 \le x \le 28{,}125$ at. %) alloys within different approaches to geometry optimization. The paper is organized as follows. Section 2 presents the details of *ab initio* calculations. Section 3 contains

the main results and discussion. Conclusions are provided at the end of the article (Section 4).

1. Calculation details

Ab initio calculations were performed by using the projector augmented wave (PAW) method implemented in the Vienna *ab initio* simulation package (VASP) [20, 21]. The exchange-correlation effects were treated in generalized gradient approximation (Perdew–Burke–Ernzerhof formalization [22]). Pseudopotentials were taken for the following electronic configurations: Fe($3p^6 3d^7 4s^1$) and Ge($4s^2 4p^2$). Kinetic energy cut-off was 450 eV, and kinetic energy cut-off for the augmentation charges was 800 eV. The Brillouin zone integration was performed by the Monkhorst–Pack scheme [23] with 8×8×8 *k*-point sampling. The calculations were converged with the energy accuracy of 10^{-7} eV. The geometry optimization of 32-atom supercells was carried out with the help of electronic and ionic relaxation. In the case of electronic relaxation, the equilibrium lattice parameters a_0 were obtained from the dependency of total energy E on the cell volume with a fitting to the Birch–Murnaghan equation of states. While the ionic optimization was fulfilled assuming that the cell shapes and ions degrees of freedom were fixed. The following phases in $Fe_{100-x}Ge_x$ ($12{,}5 \le x \le 28{,}125$ at. %) alloys, which were observed experimentally, were considered: A2 (α-Fe-type structure, space group $Im\bar{3}m$ no. 229), B2 (CsCl-type structure, space group $Pm\bar{3}m$ no. 221), $D0_3$ (BiF_3-type structure, space group $Fm\bar{3}m$ no. 225), and $L1_2$ (Cu_3Au-type structure, space group $Pm\bar{3}m$ no. 221). To create off-stoichiometric compositions in 32-supercell for each structure, either Fe or Ge atoms were replaced by Ge or Fe on randomly chosen lattice sites, respectively. This allowed us to change the composition with the step of 3,125 at. %.

After obtaining the lattice constants, we calculated the elastic moduli for cubic structures using strain tensors, which correspond to isotropic, orthorhombic, and monoclinic deformations. We assumed that the volume of the unit cell was constant, and the distortion parameter changed in the range of ±3 %. Additional calculation details can be found in [24].

2. Calculation results

The calculated equilibrium lattice parameters a_0, total energies per atom E_0, and formation energies E_{form} for electronic and ionic relaxation are presented in Table. The formation energy can be defined as a difference between the total energy per atom of an alloy and total energies per atom of its components in their equilibrium bulk structures:

$$E_{\text{form}} = E_0\left(\text{Fe}_{100-x}\,\text{Ge}_x\right) - 32\left[\left(100-x\right)E_{at}^{\text{Fe}}\left(\text{Fe}\right) + xE_{at}^{\text{Ge}}\right]/100,$$

where $E_{at}^{\text{Fe(Ge)}}$ is the total energy per atom of alloys components, x is the Ge content concentration. For A2, B2, $D0_3$, and $L1_2$ cubic structures, the lattice parameter increases with Ge content. In the case of B2 and $D0_3$ phases, the lattice constant decreases for systems with an excess of Ge ($x > 25$ at. %). For the comparison, the experimentally obtained lattice constants are also included in Table. For both relaxations, the values of lattice parameters are in good agreement with each other and with experimental results. The difference between a_0^{el} and a_0^{ion} is less than 0,5 %, and between a_0^{el} and a_0^{exp} is approximately 1 %. The differences between the obtained total energy values are negligible, and the $D0_3$ structure is energetically favorable for all considered Ge concentrations.

B2, $D0_3$, and $L1_2$ structures are stable because their formation energies are negative ($E_{\text{form}} < 0$). A2 phase is stable at Ge content $x < 18$ at. %. However, in the disordered A2 structure, the arrangement of atoms in the lattice has a significant effect on the ground state properties and formation energy, and we considered only one configuration.

Fig. 1(a) shows the atomic volume V_a as a function of Ge concentration in the range of $12{,}5 \le x \le 28{,}125$ at. %. The available experimental values [6, 9, 10] for the A2 structure are also presented in Fig. 1(a). The closest to the experiment are A2 phase results obtained with electronic relaxation and Ge content of up to $x = 21{,}875$ at. %. In the range of $x > 22$ at. %, the experimental volume changes slightly, while the theoretical estimation continues to increase. The lowest and the largest V_a are observed for the most stable phase $D0_3$ and A2 structure, respectively. The V_a of the B2 structure is close to $D0_3$. Under the transition from disordered to ordered state, the unit-cell parameters decrease slightly and, therefore, the atomic volume also decreases [25–27]. The obtained dependencies of V_a on Ge content correspond to the sequence of phase transitions observed experimentally [5, 13]:

A2→B2→$D0_3$ (8≤ x ≤22 at. %). The *fcc* phase $L1_2$ in the range of 21,875 ≤ x ≤ 28,125 at. % has a minimum of V_a in stoichiometric composition $Fe_{75}Ge_{25}$, which is in agreement with the experimental data [11]. The $L1_2$ phase is experimentally observed in the narrow Ge concentration range $x \approx 22 \div 25{,}7$ at. % [5, 11, 28, 29]. Here, we simulated a wider range of concentrations for the $L1_2$ phase, since the minimal concentration step in the 32-atoms supercell is 3,125 at. %.

Table

Optimized lattice constant a_0 (Å), total energy E_0 (eV/atom), and formation energy E_{form} (m*eV/atom*) of $Fe_{100-x}Ge_x$ alloys in comparison with experimental data (a_0^{exp}). The positive values of formation energy are bolded

x	Phase	Electronic relaxation			Ionic relaxation			a_0^{exp}
		a_0^{el}	E_0	E_{form}	a_0^{ion}	E_0	E_{form}	
12,5	A2	2,874	–7,803	–12,845	2,867	–7,802	–11,566	2,885 (13,03 at.%)[1]
	B2	2,865	–7,809	–18,965	2,857	–7,809	–19,022	
	$D0_3$	5,72	–7,851	–60,717	5,707	–7,851	–60,709	
15,625	A2	2,879	–7,680	–6,744	2,873	–7,680	–6,697	2,885 (16,13 at.%)[1], 2,891 (14 at.%)[2]
	B2	2,865	–7,695	–22,112	2,862	–7,696	–22,087	
	$D0_3$	5,720	–7,743	–69,712	5,708	–7,743	–69,665	
18,75	A2	2,889	–7,556	**0,718**	2,883	–7,556	**0,737**	2,899 (20 at.%)[2]
	B2	2,870	–7,580	–23,354	2,863	–7,580	–23,306	
	$D0_3$	5,722	–7,636	–79,794	5,709	–7,636	–78,904	
21,875	A2	2,898	–7,418	**21,643**	2,890	–7,418	**22,019**	2,902 (22.5 at.%)[2] 2,885 (21 at.%)[3]
	B2	2,868	–7,462	–22,965	2,860	–7,463	–23,219	
	$D0_3$	5,725	–7,530	–90,285	5,711	–7,529	–89,203	
	$L1_2$	3,640	–7,505	–65,941	3,633	–7,505	–65,358	
25	A2	2,909	–7,275	**47,329**	2,903	–7,275	**47,684**	2,903 (25 at.%)[2]
	B2	2,867	–7,343	–19,991	2,861	–7,343	–19,911	
	$D0_3$	5,720	–7,423	–100,095	5,707	–7,423	–100,083	
	$L1_2$	3,638	–7,413	–90,031	3,629	–7,412	–89,481	3,665[4]
28,125	A2	2,920	–7,135	**70,431**	2,914	–7,136	**70,408**	2,901 (27,5 at.%)[2]
	B2	2,867	–7,218	–12,121	2,860	–7,218	–12,141	
	$D0_3$	5,716	–7,277	–71,689	5,707	–7,277	–70,947	
	$L1_2$	3,655	–7,247	–41,225	3,649	–7,247	–41,201	3,668[4] (26,3 at.%)

[1] Data were taken from [6].
[2] Data were extrapolated from [10].
[3] Data were taken from [7].
[4] Data were taken from [11].

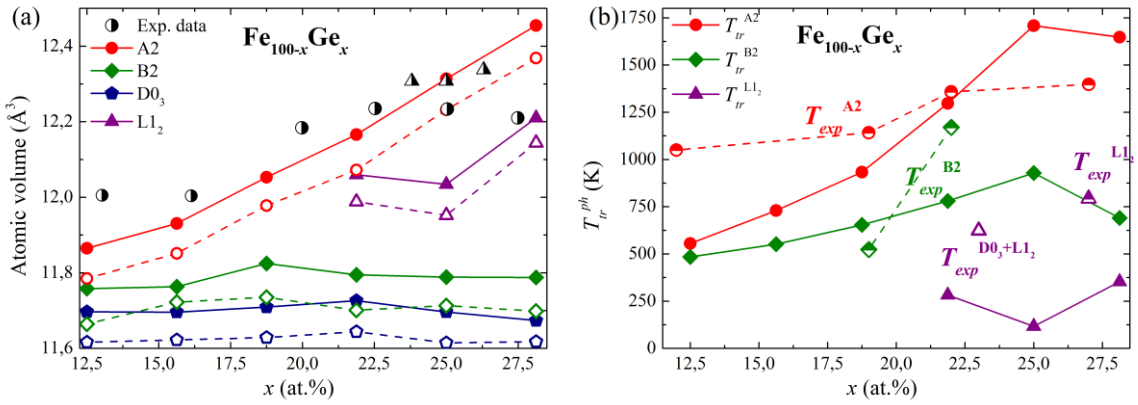

Fig. 1. Dependence of (a) $Fe_{100-x}Ge_x$ atomic volume V_a, and (b) calculated temperatures of structural phase transitions on Ge concentration, x. Atomic volumes $V_a(x)$ were obtained by two types of relaxations: electronic (filled symbols) and full ionic (open symbols). Experimental atomic volumes (half-filled symbols) for A2 (circles) and $L1_2$ (triangles) structures were taken from [6, 9–11]. The experimental values of T_{tr} were taken from [8, 11–13]

Fig. 1 (b) presents the calculated temperatures of structural phase transitions T_{tr}^{ph} as a function of Ge concentration and their comparison with the available experimental data [8, 11–13]. The estimations of T_{tr}^{ph} can be obtained from $\Delta E \approx k_B T_{tr}^{ph}$, where $\Delta E = E_0 - E_{min}$, E_{min} is the energy of the most energetically favorable structure ($D0_3$ in this case), and k_B is the Boltzmann constant. The structural phase transition temperature is the temperature, above which the corresponding phase exists. For all considered structures, T_{tr}^{ph} values increase with Ge concentration. The slope of the theoretical $T_{tr}^{A2}(x)$ curve is steeper than the experimental one. For $x > 22$ at. %, the experimental T_{exp}^{A2} curve changes slightly, while the theoretical estimation of T_{tr}^{A2} continues to increase up to 25 at. % of Ge. For the B2 structure, the experimental T_{exp}^{B2} curve increases more rapidly than the theoretical one. The pure structure $L1_2$ is experimentally observed at about 25 at. % of Ge content (through the $D0_{19} \rightarrow L1_2$ transition). The range $22 \le x \le 27$ at. % is characterized by different mixtures of the B2, $D0_3$, $D0_{19}$, and $L1_2$ phases [5, 8, 13].

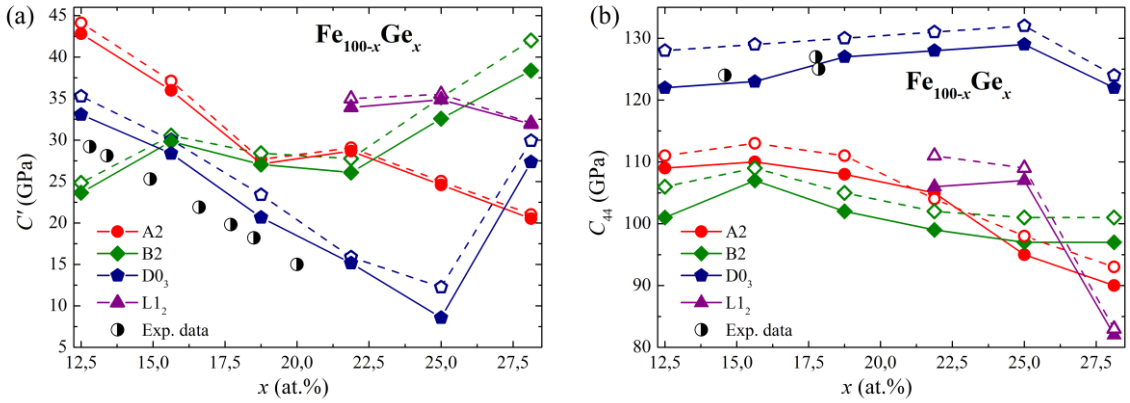

Fig. 2. Dependence of (a) tetragonal *C′* and (b) rhombohedral C_{44} shear moduli of $Fe_{100-x}Ge_x$ alloys on Ge concentration, *x*. The results were obtained by two types of relaxations: electronic (filled symbols) and full ionic (open symbols). Experimental values (half-filled symbols) were taken from [1] for *C′* and from [14] for C_{44}

The concentration dependencies of tetragonal C' and rhombohedral C_{44} shear moduli are presented in Fig. 2 (a, b) together with the room-temperature experimental results. For both elastic moduli, the closest to the experimental values were calculation results for the $D0_3$ structure obtained by electronic relaxation. The increase of Ge concentration up to x = 25 at. % leads to a decrease in the tetragonal elastic modulus. This indicates a pronounced softening of the $D0_3$ structure. The rhombohedral shear modulus C_{44} does not change significantly with x, only slightly decrease for structures with Ge excess ($x > 25$ at. %). The same concentration dependencies for both C' and C_{44} were obtained theoretically for the $D0_3$ phase in the Fe-Ga system [24]. In the case of A2 and $L1_2$ structures, the tetragonal shear modulus decreases in the considered range of $12{,}5 \le x \le 28{,}125$ at.%. For A2, B2, and $L1_2$ structures, the rhombohedral shear modulus C_{44} has a trend similar to C'.

Conclusion

We have studied the structural and elastic properties of Fe-Ge alloys by using the first-principles methods. Crystal structure optimization was performed for phases A2, B2, $D0_3$, and $L1_2$ of $Fe_{100-x}Ge_x$ ($12{,}5 \le x \le 28{,}125$ at. %). We considered two types of relaxations: electronic and full ionic. We showed that the lattice constants increase with Ge concentration in both approaches, and the difference between obtained lattice constant, total energy, and formation energy is negligible. The $D0_3$ structure is energetically favourable for all considered Ge concentrations. The dependence of atomic volume $V_a(x)$ on Ge content corresponds to the sequence of phase transitions observed experimentally ($A2 \rightarrow B2 \rightarrow D0_3$) in the range $8 \le x \le 22$ at. %. We estimated the temperature of structural phase transitions T_{tr}^{ph} as a function of Ge concentration and found that the slope of the calculated curve for the A2 phase is steeper than for the experimental one. Moreover, we obtained the dependencies of tetragonal C' and rhombohedral C_{44} shear

moduli on Ge content. For A2, $D0_3$, and $L1_2$ structures the increase of Ge concentration leads to a decrease in the tetragonal elastic moduli. The rhombohedral shear moduli do not change significantly with *x*. In general, results obtained by electronic relaxation are in good agreement with the experimental data.

Acknowledgments

This work was supported by Russian Science Foundation grant No. 18-12-00283 (Sections 2 and 3), V. Sokolovskiy and V. Buchelnikov gratefully acknowledge the financial support of Ministry of Science and Higher Education of the Russian Federation in the framework of increase Competitiveness Program of NUST "MISIS" (Grant No. K2-2019-006), implemented by a governmental decree dated 16th of March 2013, No 211, M. Zagrebin acknowledge the financial support of Young Scientist Support Foundations of Chelyabinsk State University.

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Received March 16, 2020

Bulletin of the South Ural State University
Series "Mathematics. Mechanics. Physics"
2020, vol. 12, no. 2, pp. 49–56

УДК 538.91 **DOI: 10.14529/mmph200206**

СТРУКТУРНЫЕ И УПРУГИЕ СВОЙСТВА СПЛАВОВ FE-GE: ИССЛЕДОВАНИЯ *AB INITIO*

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В работе представлены исследования структурных и упругих свойств фаз A2, B2, $D0_3$ и $L1_2$ сплавов $Fe_{100-x}Ge_x$ ($12{,}5 \le x \le 28{,}125$ ат. %), выполненные при помощи теории функционала плотности. Кристаллические структуры исследовались при помощи двух типов релаксаций: электронной и полной ионной. Построены концентрационные зависимости атомных объемов, температур структурных фазовых переходов, тетрагональных и ромбоэдрических модулей сдвига. Кривые зависимостей величин атомного объема соответствует последовательности фазовых переходов, наблюдаемых экспериментально: A2 → B2 → $D0_3$ ($x \le 22$ ат. % содержания Ge). Показано, что температуры структурных фазовых переходов возрастают с увеличением концентрации Ge. В соответствии с экспериментальными результатами рассчитанные тетрагональные модули для структур $D0_3$, A2 и $L1_2$ уменьшаются с ростом атомов Ge в сплавах. Величина ромбоэдрического модуля сдвига существенно не изменяется с увеличением числа атомов Ge. C_{44} увеличивается для фазы $D0_3$, в то время как для A2, B2 и $L1_2$ уменьшается.

Ключевые слова: ab initio; кристаллическая структура; фазовые превращения; упругие модули.

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Поступила в редакцию 16 марта 2020 г.