

ELECTRICAL AND MAGNETIC PROPERTIES

First-Principles Simulation of an Ordered Sigma Phase of the Fe–Cr System in the Ferromagnetic State

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Abstract—Results of a first-principles simulation of the σ phase of the Fe–Cr system performed using a WIEN2k program code in the generalized-gradient approximation for the exchange-correlation potential are given. The work was aimed at the determination of equilibrium states and energies of formation of the ferromagnetic state of the σ phase of the Fe–Cr system, whose structure (space group no. 136) was examined in the form of ordered configurations $A_2B_4C_8D_8E_8$, where A , B , C , D , and E are the crystallographic nonequivalent atomic subgroups, and the subscripts indicate their size (number of atoms). The calculations performed show that two most stable configurations $Fe_2Cr_4Fe_8Fe_8Cr_8$ ($x_{Cr} = 0.40$) and $Fe_2Fe_4Cr_8Fe_8Cr_8$ ($x_{Cr} = 0.53$) in the ferromagnetic state are more stable than in the nonmagnetic state. The influence of ferromagnetism on the value of the energy of formation calculated relative to the pure components in their thermodynamically stable states is especially noticeable in the case of the configuration $Fe_2Cr_4Fe_8Fe_8Cr_8$ ($x_{Fe} = 0.60$) (approximately 6.36 kJ/mol). In this case, the average atomic magnetic moment was approximately $0.75 \mu_B$. The results of the first-principles calculations (at 0 K) of the energies of formation and magnetic moments of the ordered configurations of the σ phase satisfactorily agree with the available experimental data.

Key words: first-principles simulation, Fe–Cr alloy, ferromagnetism

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1. INTRODUCTION

In 1923 Bain for the first time revealed the precipitation of a hard nonmagnetic phase in the Fe–Cr system, which was later called the “sigma phase.” The process of its formation was sufficiently slow, and the phase was observed in the Fe–Cr system for the composition of approximately 1 : 1 even after a prolonged high-temperature annealing. In the early 1960s, the precipitation of the σ phase was discovered in the nickel alloys, and later similar phenomena were noted also in a number of other high-temperature high-strength alloys. This drew an enhanced attention of metallurgists, since the σ phase proved to be a very brittle and stable compound, whose presence led to a noticeable deterioration of properties of these materials. An additional negative influence on the mechanical properties of materials comes also from the lamellar morphology of the σ phase, which is characteristic of the class of compounds with a topologically close-packed structure (tcp phases) [1].

The sigma phase, as any tcp phase, contains a large quantity of refractory elements and in the Fe–Cr system it is formed for the composition near 1 : 1. Its unit cell contains 30 atoms distributed in five crystallographically nonequivalent subgroups (space group no. 136)

[2]. The precise coordinates of the atomic positions in the unit cell and the percentage relationship between the Fe and Cr atoms in each of the sublattices are known from the experiment. Each nonequivalent subgroup of the unit cell contains atoms of both types. Consequently, for the simulation of this “mixed” unit cell it is necessary to consider all 30 atoms as being nonequivalent, and the number of possible configurations of the arrangement of atoms is very large. Unfortunately, the conduction of calculations in this scheme is quite difficult. Therefore, at present the researchers restrict themselves to the study of ordered configurations of the σ phases in the form of $A_2B_4C_8D_8E_8$, where each of the sublattices is occupied with atoms of only one type (Fe or Cr) [3, 4]; A , B , C , D , and E are crystallographically nonequivalent subgroups, and the subscripts indicate their size (number of atoms), respectively. Among these 32 ordered complexes, we can select the most stable ones and use them to determine the σ -phase characteristics of interest for us. In this case, two circumstances should be taken into account. The first consists in the fact that the experimental values of the lattice parameters employed in the previously published computational works [4, 5] are, generally speaking, not equilibrium for ordered complexes of the

σ phase in question. Consequently, the search for the equilibrium states of these configurations remains a problem to be solved.

And, in the second place, until recently [6] in the computational works the σ phase was usually considered as nonmagnetic in the entire temperature range [4, 5], since at room temperature it is precisely nonmagnetic [7]. However, according to [8, 9] the σ phase can possess weak ferromagnetism with a Curie temperature below 60 K depending on the alloy composition. Consequently, it is of interest to verify the possibility of formation and stability of the σ phase in Fe–Cr system in the ferromagnetic state. Thus, this study was aimed at determining the equilibrium states of the ordered configurations of the σ phase in the Fe–Cr system and analyzing the influence of ferromagnetism on the stability of this phase.

2. EXPERIMENTAL

To solve this problem, we employ the first-principles method of calculation of the electron structure using a WIEN2k program code [10], in which the equations of the well-known density-functional theory (DFT) are solved using the spin-polarized full-potential method of the linearized augmented plane waves [11] in the generalized-gradient approximation [12] for describing the exchange-correlation potential. The experimental values of the lattice parameters of the σ phase are $V = 2380.4821 \text{ au}^3$ and $c/a = 0.5182$ [2]. The radii of the muffin-tin orbital R_{mt} for the Fe and Cr atoms are assumed to be 1.89 and 1.81 au, respectively. The product of the minimum radius of the muffin-tin orbital and the maximum reciprocal-lattice vector is $R_{\text{mt}}K_{\text{max}} = 8.50$, and the number of k points in the first Brillouin zone is taken to be $N_k = 512$.

3. RESULTS AND DISCUSSION

3.1. Equilibrium State. Energy of Formation

The sigma phase has a tetragonal crystal lattice and, therefore, its equilibrium state depends not only on the volume of the unit cell V , but also on the axial ratio c/a . Thus, the search for the equilibrium state of the σ -phase crystal lattice is the problem of optimization that depends on two parameters. After it is solved for the obtained equilibrium states of the ordered configurations of the σ phase, according to the aim stated in this work, it is necessary to find the appropriate energies of formation, which are determined from the following formula:

$$\Delta^{\alpha\alpha} E^{\sigma}(x_B = \text{const}, 0 \text{ K}) = E_{\text{tot}}^{\sigma}(x_B, 0 \text{ K}) - [x_A E_{\text{tot}, A}^{\alpha}(0 \text{ K}) + x_B E_{\text{tot}, B}^{\alpha}(0 \text{ K})], \quad (1)$$

where $\Delta^{\alpha\alpha} E^{\sigma}(x_B = \text{const}, 0 \text{ K})$ is the energy of formation of the chemical (ordered) compound $A_{x_A} B_{x_B}$, $E_{\text{tot}}^{\sigma}(x_B, 0 \text{ K})$ is the total energy of the compound; $E_{\text{tot}, A}^{\alpha}(0 \text{ K})$ and

$E_{\text{tot}, B}^{\alpha}(0 \text{ K})$ are the total energies of pure components in the thermodynamically stable states (ferromagnetic and antiferromagnetic states with a body-centered crystal structure for iron and chromium, respectively); and x_A and x_B the concentrations of the compound components (in molar fractions). The thus-obtained equilibrium states and the corresponding energies of formation of the ordered configurations of the σ phase are given in Table 1 together with the values of the energy of formation determined earlier without the optimization of the lattice parameters. We calculated only three ordered complexes of the σ phase, since, according to [4], the most stable configurations will be the following ones: $\text{Fe}_2^{12} \text{Fe}_4^{15} \text{Cr}_8^{14} \text{Fe}_8^{12} \text{Cr}_8^{14}$ ($x_{\text{Cr}} = 0.53$) and $\text{Fe}_2^{12} \text{Cr}_4^{15} \text{Fe}_8^{14} \text{Fe}_8^{12} \text{Cr}_8^{14}$ ($x_{\text{Cr}} = 0.40$). The complex $\text{Fe}_2^{12} \text{Fe}_4^{15} \text{Fe}_8^{14} \text{Fe}_8^{12} \text{Cr}_8^{14}$ ($x_{\text{Cr}} = 0.27$) was examined for comparison and analysis of the results obtained for other two configurations, since the nucleation of the σ phase can start with $x_{\text{Cr}} = 0.27$. As can be seen from Table 1, in the first approximation, without the determination of the equilibrium state, the selected ordered configurations of the σ phase under the assumption of the ferromagnetic state are more stable in comparison with the nonmagnetic state examined earlier in the works devoted to the first-principles simulation of the σ phase [3–5]. In the case of configuration $\text{Fe}_2^{12} \text{Fe}_4^{15} \text{Cr}_8^{14} \text{Fe}_8^{12} \text{Cr}_8^{14}$ ($x_{\text{Cr}} = 0.53$), the influence of ferromagnetism is weak; for the configurations $\text{Fe}_2^{12} \text{Cr}_4^{15} \text{Fe}_8^{14} \text{Fe}_8^{12} \text{Cr}_8^{14}$ ($x_{\text{Cr}} = 0.40$) and $\text{Fe}_2^{12} \text{Fe}_4^{15} \text{Fe}_8^{14} \text{Fe}_8^{12} \text{Cr}_8^{14}$ ($x_{\text{Cr}} = 0.27$), a considerable decrease in the energy of formation (by a value several times greater than the accuracy of calculations) was noted. This is apparently due to the high concentration of iron atoms connected via strong exchange interaction of the ferromagnetic type.

It is also seen from Table 1 that the use of ordered configurations in the calculations of equilibrium states leads to a larger change in the energy of formation for the $\text{Fe}_2^{12} \text{Fe}_4^{15} \text{Cr}_8^{14} \text{Fe}_8^{12} \text{Cr}_8^{14}$ ($x_{\text{Cr}} = 0.53$) than for the $\text{Fe}_2^{12} \text{Cr}_4^{15} \text{Fe}_8^{14} \text{Fe}_8^{12} \text{Cr}_8^{14}$ ($x_{\text{Cr}} = 0.40$) configuration. This can be understood if we compare the calculated lattice parameters for these configurations with experimentally measured values [2]. In the case of the configuration $\text{Fe}_2^{12} \text{Fe}_4^{15} \text{Cr}_8^{14} \text{Fe}_8^{12} \text{Cr}_8^{14}$ ($x_{\text{Cr}} = 0.53$), the equilibrium volume V_{eq} and axial ratio $(c/a)_{\text{eq}}$ differ from the experimental values by 5.95% and 3.0%, respectively, and for the configuration $\text{Fe}_2^{12} \text{Cr}_4^{15} \text{Fe}_8^{14} \text{Fe}_8^{12} \text{Cr}_8^{14}$ ($x_{\text{Cr}} = 0.40$), by 5.44% and 0.50%. The energy of formation of the latter complex is less than for the other two configurations. Thus, the lattice parameters of this complex better satisfy the experimental values, and we can assume that the configuration $\text{Fe}_2^{12} \text{Cr}_4^{15} \text{Fe}_8^{14} \text{Fe}_8^{12} \text{Cr}_8^{14}$ ($x_{\text{Cr}} = 0.40$) is a more adequate model of the real σ phase.

Table 1. Energies of formation $\Delta^{\alpha\alpha}E^{\sigma}$ of three atomically ordered configurations of the σ phase for the experimental [2] and equilibrium values of the lattice parameters

Configuration of the σ phase	x_{Cr}	V , au ³ /cell	c/a	$\Delta^{\alpha\alpha}E^{\sigma}$, kJ/mol
Experimental values of lattice parameters [2]				
FeFeFeFeCr(NM)	0.27	2380.4821	0.5182	22.28
FeFeFeFeCr(FM)				9.89
FeCrFeFeCr(NM)	0.40	2380.4821	0.5182	15.28
FeCrFeFeCr(FM)				8.92
FeFeCrFeCr(NM)	0.53	2380.4821	0.5182	10.57
FeFeCrFeCr(FM)				9.97
Equilibrium values of lattice parameters (this work)				
FeFeFeFeCr(FM)	0.27	2272.7646	0.5233	8.52
FeCrFeFeCr(FM)	0.40	2250.9832	0.5208	6.83
FeFeCrFeCr(FM)	0.53	2238.4821	0.5027	7.21

Designations: NM and FM stand for the nonmagnetic and ferromagnetic states of the σ phase, respectively. The indices in the designations of configurations are omitted for simplicity.

Table 2. Average magnetic moments at the atoms of crystallographically nonequivalent sublattices and total unit cell of the structure of the σ -phase in $\mu(\mu_{\text{B}})$ for three atomically ordered configurations in the equilibrium states

Configuration of the σ -phase	x_{Cr}	μ /sublattice, $\mu(\mu_{\text{B}})$					μ /unit cell, $\mu(\mu_{\text{B}})$
		A	B	C	D	E	
FeFeFeFeCr	0.27	1.27	2.15	1.91	1.43	-0.43	1.15
FeCrFeFeCr	0.40	0.85	-0.31	1.81	1.16	-0.23	0.75
FeFeCrFeCr	0.53	0.70	1.54	-0.21	0.31	-0.12	0.25

Note: Indices in the designations of configurations are omitted for simplicity.

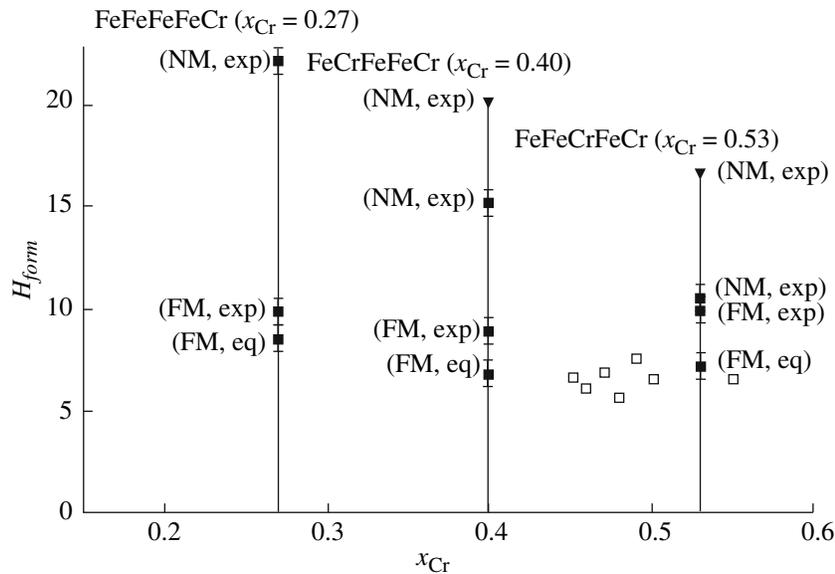


Fig. 1. Energies of formation $\Delta^{\alpha\alpha}E^{\sigma}$ ($x_B = \text{const}$, 0 K) of three atomically ordered configurations of the σ phase $\text{Fe}_2\text{Cr}_4\text{Fe}_8\text{Fe}_8\text{Cr}_8$ ($x_{\text{Cr}} = 0.27$), $\text{Fe}_2\text{Cr}_4\text{Fe}_8\text{Fe}_8\text{Cr}_8$ ($x_{\text{Cr}} = 0.40$), and $\text{Fe}_2\text{Fe}_4\text{Cr}_8\text{Fe}_8\text{Cr}_8$ ($x_{\text{Cr}} = 0.53$) with respect to the pure components with the bcc structure; designations in the parentheses: FM, NM, ferromagnetic and nonmagnetic state; exp, eq, experimental and equilibrium values of the lattice parameters of the corresponding configuration; horizontal line bars in the graph designate the error bounds of calculations; (\square) experimental data for the enthalpy of formation H_{form} [15] (304 K); (\blacktriangledown) the earlier results of first-principles calculations [4] (0 K), and (\blacksquare) the results of this work (0 K).

The values of the average magnetic moment at an atom of the total unit cell obtained in this case and at an atom of each of the crystallographically nonequivalent sublattices of the σ phase (for all configurations) are given in Table 2. It can be assumed that the result obtained (at 0 K) satisfactorily agrees with the existing experimental value, which is approximately $0.20 \mu_B$ at a temperature of 4 K [8].

Figure 1 compares our values of the energy of formation with the previously published results of other authors [4] and available experimental data [13]. The results given in [4] were also obtained with the aid of the first-principles procedure of the simulation of electron structure (at 0 K), but with allowance for only the nonmagnetic state of the σ phase and without the determination of the equilibrium states of its ordered configurations. It is evident that the allowance for the effect of ferromagnetism on the energy of formation makes it possible to attain a better agreement with the experimental data in comparison with [4].

Density of States

When speaking of the magnetism of a system, we should consider the behavior of the density of states. Since, according to the phase diagram, the σ phase is formed from the ferromagnetic α phase [14], it was of interest to compare the behavior of the density of states of the Fe–Cr system in both phases, which were calculated also with the aid of the method indicated in Section 2. In the case of the α phase of the Fe–Cr system (see Fig. 2), it can be assumed that the density of states

in it is close to the simple superposition (addition) of the densities of states of pure components with a bcc structure. Note that there is observed a small difference in the densities of states for the electrons with the oppositely directed spins, which indicates the known phenomenon of the ferromagnetism of the Fe–Cr solid solution with the bcc structure [15, 16]. The clearly pronounced peaks of the α phase start filling up with going to the density of states of the σ phase (Fig. 3). This change in the density of states corresponds to a substantial change in the magnetic structure of the σ phase of the Fe–Cr system. The average magnetic moment at Cr atoms with going from the α - into the σ phase reverses sign from $\mu_{\text{Cr}}^{\alpha} = +0.55 \mu_B$ to $\mu_{\text{Cr}}^{\sigma} = -0.25 \mu_B$ and $\mu_{\text{Cr}}^{\sigma} = -0.33 \mu_B$ for the configurations $\text{Fe}_2^{12}\text{Cr}_4^{15}\text{Fe}_8^{14}\text{Fe}_8^{12}\text{Cr}_8^{14}$ ($x_{\text{Cr}} = 0.40$) and $\text{Fe}_2^{12}\text{Fe}_4^{15}\text{Cr}_8^{14}\text{Fe}_8^{12}\text{Cr}_8^{14}$ ($x_{\text{Cr}} = 0.53$), respectively. Thus, the magnetic moments at chromium atoms in the σ phase begin orienting antiparallel to the magnetic moments at iron atoms. It is supposed that the related decrease in energy leads to a reduction in the energy of formation of the magnetically ordered σ phase.

4. CONCLUSIONS

In this work, we present the results of a first-principles simulation performed with the aid of a WIEN2k computer program. When analyzing systems constructed for the consideration of the σ phase, which is of interest for us, it was found that the atomically ordered configura-

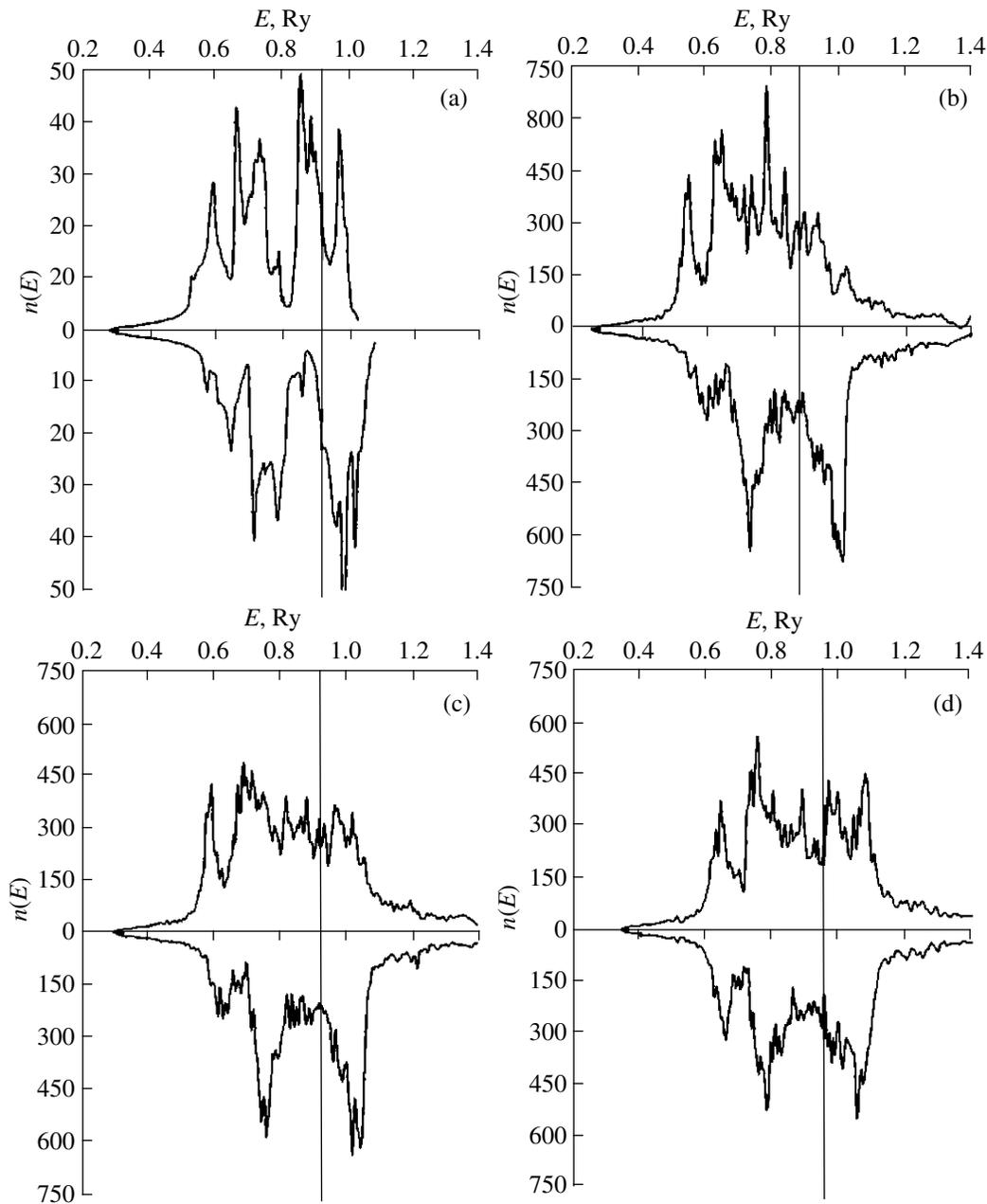


Fig. 2. Total density of states $n(E)$ of the Fe–Cr alloys in the ferromagnetic state: (a) with a body-centered cubic structure and with the structure for of the σ phase as three atomically ordered configurations; (b) $\text{Fe}_2\text{Fe}_4\text{Fe}_8\text{Fe}_8\text{Cr}_8$ ($x_{\text{Cr}} = 0.27$); (c) $\text{Fe}_2\text{Cr}_4\text{Fe}_8\text{Fe}_8\text{Cr}_8$ ($x_{\text{Cr}} = 0.40$); and (d) $\text{Fe}_2\text{Fe}_4\text{Cr}_8\text{Fe}_8\text{Cr}_8$ ($x_{\text{Cr}} = 0.533$). The position of the Fermi level E_{F} is shown by a vertical line.

rations of the σ phase in the ferromagnetic state are more stable than in the nonmagnetic state. It was revealed that these configurations possess a small average atomic magnetic moment, which satisfactorily agrees with the known experimental value [8, 9]. It was also found that the average magnetic moment at the chromium atoms changes sign upon the transition from the α - into the σ phase; i.e., the magnetic moments at the chromium atoms in the σ phase begin to be oriented antiparallel to

the magnetic moments at the iron atoms. The related decrease in energy can be responsible for the lower value of the energy of formation of the magnetically ordered σ phase.

Thus, it was shown that in the case of the atomically ordered σ phase of the Fe–Cr system it is necessary to take into account the ferromagnetic state at low temperatures (about 0 K; $T_{\text{c}} = 60$ K [8, 9]) in contrast to the pre-

viously published computational works, in which the nonmagnetic state of this phase was considered [3–5].

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