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# Electronic Structure and Ordering Degree in Fe<sub>3</sub>Al Alloy Doped with Transition Metals. *Ab Initio* Study

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Fe<sub>3</sub>Al alloy crystallizes in DO<sub>3</sub>-type structure. In the perfectly ordered alloy there are two nonequivalent sublattices (A,C) and B, which are occupied by Fe atoms, whereas all D sites are taken by metalloid. Such perfect ordering is, however, difficult to achieve experimentally, and some disorder between B–D as well as (A,C)–D sublattices typically appears in real samples. This disorder modifies strongly electronic structure and magnetic properties. The aim of this contribution is to investigate total energy dependence of atomic exchange of sites between B–D and (A,C)–D positions in Fe<sub>3</sub>Al as well as in alloys doped with transition metals using *ab-initio* technique. Furthermore, dependence of electronic and magnetic properties of Fe<sub>3</sub>Al-based alloys on the crystallographic ordering is thoroughly investigated.

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## 1. Introduction

Fe<sub>3</sub>Al doped with transition metals has been widely investigated because of its excellent oxidation and corrosion resistance at room temperature [1, 2]. Fe<sub>3</sub>Al alloy crystallizes in DO<sub>3</sub>-type structure [3]. In the perfectly ordered structure there are two nonequivalent sites of Fe: (A,C) and B, that have different local environments [4], whereas aluminium occupies D positions. However, numerous experiments indicate that it is very difficult to achieve perfect ordering and usually a small disorder between B and D as well as (A,C) and D sublattices exists. Moreover, the degree of order turns out to be dependent on the transition metal impurity. Noteworthy, the type of ordering in Fe<sub>3-x</sub>T<sub>x</sub>Al alloys, when transition metal impurities (T) are added, is very sensitive to the heat treatment procedure [5]. Small disorder present in the alloys influences strongly electronic structure as well as magnetic properties [6]. In order to explain magnetic properties of the alloys, local effects should be taken into account [7]. This problem is studied theoretically in the present paper for T = Cr and Mn.

## 2. Computational details

Electronic structure of Fe<sub>3</sub>Al, Fe<sub>2.875</sub>Cr<sub>0.125</sub>Al and Fe<sub>2.875</sub>Mn<sub>0.125</sub>Al has been studied within the framework of the local spin-density approximation, using the self-consistent spin-polarized tight-binding linear muffin-tin orbital method [8] in the atomic sphere approximation (TB-LMTO-ASA). The exchange-correlation potential was taken in the form of von Barth and Hedin [9] with the Langreth–Mehl–Hu non-local exchange correlation correction [10]. The values of the atomic sphere radii were chosen in such a way that the sum of all atomic sphere volumes was equal to the volume of the unit cell. The

initial atomic configurations for every atoms were taken to be the same as for pure elements. The tetrahedron method [11, 12] was used for integration over the Brillouin zone. Calculations were carried out for at least 280 *k*-points in the irreducible wedge of the Brillouin zone. The iterations were repeated until the energy eigenvalues of the consecutive iteration steps converged to values stable within 0.01 mRy. Electronic structure calculations were carried out using spin-polarized (ferromagnetic) approach. The supercell structure with 32 atoms was used in calculations. Supercell was constructed by repetition of the crystal cell positions along the main diagonal. The used lattice parameters were the experimental ones [13, 14].

## 3. Fe<sub>3</sub>Al

Total energy calculations indicate on tendency of complete crystallographic ordering in Fe<sub>3</sub>Al alloy (Table I). This result contradicts many experimental findings [15–18]. It turns out that dislocations are easily formed in the real system. This in turn disturbs the ordering [19]. However, having assumed in calculations a small disorder between B and D sublattices consisting in an exchange of positions of one iron and one aluminium atoms in supercell, the total energy increases by 9 mRy/atom with respect to the minimal value. If one allows for (A,C)–D-type disorder, this leads to an increase of total energy by at least 39 mRy/atom.

Exchange of positions Fe(B–D) and Al(D–B) causes an increase of total magnetic moment from 6.21  $\mu_B$  to 6.29  $\mu_B$ . Analogical exchange between (A,C) and D sublattices leads to even higher value of total magnetic moment 6.51  $\mu_B$ . Magnetic moments of Fe(D), for both types of disorder, are higher than magnetic moment of Fe(B), which is connected with different atomic composition of second coordination sphere around D-sites. The latter contains more iron atoms and, in consequence, exhibits higher magnetic moment. Assuming B–D type of

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disorder, aluminium locates in B and D sublattices, thus additional Al can be locally found in the first coordination sphere of Fe(A,C). However, in average the composition of the first coordination sphere of Fe(A,C) remains the same as in ordered Fe<sub>3</sub>Al (the nearest neighbourhood 1NN = 4Fe, 4Al) and average magnetic moment of

Fe(A,C) does not change significantly. On the contrary, composition of second and third coordination sphere of Fe(B) changes in B–D type of disorder: 2NN contains less Al, whereas 3NN more Al than in ordered Fe<sub>3</sub>Al. It leads to a small increase of Fe(B) magnetic moment from 2.46  $\mu_B$  to 2.49  $\mu_B$ .

TABLE I

Results of total energy calculations, total magnetic moments ( $\mu_B$  per formula unit) and average atomic magnetic moments ( $\mu_B$  per atom) in Fe<sub>3</sub>Al;  $\Delta E$  — difference between the total energy of the considered configuration and minimal total energy (per atom).

Fe <sub>3</sub> Al		$\Delta E$	$\mu_{\text{total}}$	$\mu_{\text{Fe(A,C)}}$	$\mu_{\text{Fe(B)}}$	$\mu_{\text{Fe(D)}}$	$\mu_{\text{Al(D)}}$	$\mu_{\text{Al(B)}}$	$\mu_{\text{Al(A,C)}}$
ordered		0	6.21	1.95	2.46	–	–0.15	–	–
disorder B–D		9 mRy	6.29	1.96	2.49	2.66	–0.14	–0.12	–
disorder (A,C)–D		39 mRy	6.51	2.11	2.39	2.49	–0.14	–	–0.16

TABLE II

Results of the total energy calculations, total ( $\mu_B$  per formula unit) and average atomic magnetic moments ( $\mu_B$  per atom) in Fe<sub>2.875</sub>Cr<sub>0.125</sub>Al.  $\Delta E$  — difference between the total energy of the considered configuration and minimal total energy (per atom).

Fe <sub>2.875</sub> Cr <sub>0.125</sub> Al		$\Delta E$	$\mu_{\text{total}}$	$\mu_{\text{Fe(A,C)}}$	$\mu_{\text{Fe(B)}}$	$\mu_{\text{Fe(D)}}$	$\mu_{\text{Cr}}$	$\mu_{\text{Al(D)}}$	$\mu_{\text{Al(B)}}$	$\mu_{\text{Al(A,C)}}$
Cr	ordered	0	5.37	1.79	2.42	–	–1.54	–0.13	–	–
(B)	disorder B–D	1 mRy	5.54	1.81	2.53	2.70	–1.34	–0.13	–0.14	–
	disorder (A,C)–D	44 mRy	5.85	1.97	2.43	2.58	–1.32	–0.13	–	–0.12
Cr	ordered	25 mRy	5.73	1.99	2.40	–	–2.28	–0.14	–	–
(A,C)	disorder B–D	24 mRy	5.72	1.96	2.44	2.55	–2.25	–0.13	–0.12	–
	disorder (A,C)–D	52 mRy	5.93	2.11	2.35	2.37	–2.16	–0.13	–	–0.15

TABLE III

Results of the total energy calculations, total ( $\mu_B$  per formula unit) and average atomic magnetic moments ( $\mu_B$  per atom) in Fe<sub>2.875</sub>Mn<sub>0.125</sub>Al.  $\Delta E$  — difference between the total energy of the considered configuration and minimal total energy (per atom).

Fe <sub>2.875</sub> Mn <sub>0.125</sub> Al		$\Delta E$	$\mu_{\text{total}}$	$\mu_{\text{Fe(A,C)}}$	$\mu_{\text{Fe(B)}}$	$\mu_{\text{Fe(D)}}$	$\mu_{\text{Mn}}$	$\mu_{\text{Al(D)}}$	$\mu_{\text{Al(B)}}$	$\mu_{\text{Al(A,C)}}$
Mn	ordered	57 mRy	6.16	1.94	2.46	–	2.22	–0.15	–	–
(B)	disorder B–D	60 mRy	6.20	1.94	2.50	2.58	2.21	–0.15	–0.14	–
	disorder (A,C)–D	90 mRy	6.42	2.07	2.40	2.49	2.14	–0.14	–	–0.16
Mn	ordered	5 mRy	5.87	2.06	2.43	–	–2.32	–0.13	–	–
(A,C)	disorder B–D	0	5.84	2.02	2.46	2.57	–2.39	–0.13	–0.11	–
	disorder (A,C)–D	23 mRy	6.01	2.15	2.38	2.42	–2.37	–0.13	–	–0.15

When (A,C)–D type of disorder is present in the alloy, then additional Al can locate in the first coordination sphere of Fe(B) and it causes a decrease of Fe(B) magnetic moment from 2.46  $\mu_B$  to 2.39  $\mu_B$ . In case of Fe(A,C) opposite effect takes place (there is less Al in the 1NN in comparison with ordered Fe<sub>3</sub>Al) and Fe(A,C) magnetic moment increases from 1.95  $\mu_B$  to 2.11  $\mu_B$ .

B–D type of disorder causes significantly smaller increase of Fe(A,C) and Fe(B) magnetic moments than (A,C)–D type of disorder which indicates again on the not negligible role of next nearest neighbors shells. Magnetic moments of aluminium in all sublattices are antiparallel with respect to Fe moments and their values vary from –0.12  $\mu_B$  to –0.16  $\mu_B$ .

Observed changes of the magnetic moments cannot be explained only by changes of the Wigner–Seitz sphere radii, which does not exceed 0.01 a.u. concerning different atomic arrangements.

Decreasing of ordering degree in Fe<sub>3</sub>Al alloy augments variety of local surroundings of atoms. It leads to more complicated densities of states (Fig. 1). A broadening of  $t_{2g}$  and  $e_g$  states and significant diminution of maximum DOS values upon B–D-type of disorder are visible, particularly for majority states. Furthermore, some minority states are pushed above the Fermi level which increases the difference between numbers of occupied majority and minority states in disordered alloys.

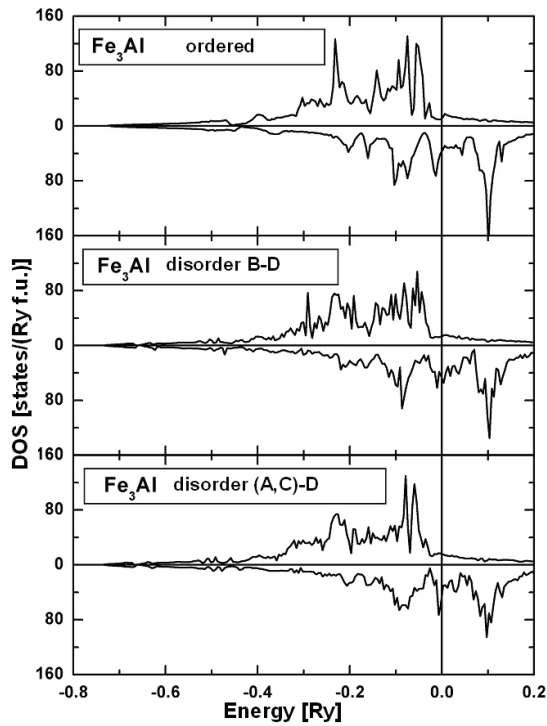


Fig. 1. Total densities of states (DOS) of  $\text{Fe}_3\text{Al}$  for crystallographically ordered configuration, as well as for B–D and (A,C)–D types of disorder.

When a small disorder between (A,C) and D sublattices is introduced, then, first of all, the density of  $t_{2g}$  states decreases, whereas two main  $e_g$  peaks remain almost unchanged. The decrease of the number of occupied minority states is manifested in an increase of the total magnetic moment. Interestingly, placing of aluminium atom in B or (A,C) positions results in appearance of very narrow energy gaps (about 0.01 Ry for majority and 0.03 Ry for minority states) in the region of low energies (about  $-0.65$  Ry). Additionally, both types of disorder lead to a small decrease of density of states of minority  $e_g$  band above the Fermi level.

#### 4. $\text{Fe}_{2.875}\text{Cr}_{0.125}\text{Al}$

According to the total energy calculations, doping  $\text{Fe}_3\text{Al}$  with the small amount of chromium does not change general ordering of alloy. Minimal total energy is obtained when all aluminium atoms occupy D sublattice, and doping chromium atom is placed in B position (Table II). However, a small B–D disorder does not introduce as large energy difference as in the case of pure  $\text{Fe}_3\text{Al}$ . In  $\text{Fe}_{2.875}\text{Cr}_{0.125}\text{Al}$  alloy it is equal to 1 mRy/atom only. When chromium atom locates in (A,C) position, then the energy difference between ordered and B–D type disordered configurations is also equal to 1 mRy/atom, but this time with the preference of disordered structure. It follows from the results presented in Table II that independently of whether chromium locates at B or

(A,C) positions, the (A,C)–D-type of disorder is less preferred.

Transfer of 12.5% of aluminium into (A,C) sublattice causes an increase of the total magnetic moment and of the average Fe(A,C) magnetic moment. As in the case of  $\text{Fe}_3\text{Al}$ , the magnetic moment of Fe(D) is higher than the magnetic moments of Fe(B) for all considered atomic configurations.

Magnetic moments of chromium are oriented antiferromagnetically with respect to the magnetic moments of iron. For each type of ordering, the value of the magnetic moment of Cr(A,C) is higher by at least 50% than the value of magnetic moment of Cr(B). Additionally, maximum values of chromium magnetic moments have been obtained for atomic configurations with all aluminium atoms located at D sublattice.

Magnetic moments of aluminium, similarly as in pure  $\text{Fe}_3\text{Al}$  depend on the local environment. If, for Cr(B) occupation, one introduces B–D-type of disorder, then chromium atom can be found in second coordination sphere of Al(D) and only in the third coordination sphere of Al(B). That's why magnetic moment of Al(B) is obtained slightly higher than the one of Al(D). When Cr occupies B-site in the presence of (A,C)–D-type of disorder, the chromium atom can be found in the first coordination sphere of Al(A,C). It causes a decrease of magnetic moment of Al(A,C) in comparison with Al(B) magnetic moment. Chromium atom located in (A,C) position leads to the opposite effects than Cr(B).

#### 5. $\text{Fe}_{2.875}\text{Mn}_{0.125}\text{Al}$

If one adds small amount of Mn to  $\text{Fe}_3\text{Al}$  alloy,  $x = 0.125$ , manganese preferentially locates in (A,C) sublattice (Table III). Furthermore, its presence introduces B–D type disorder in parent  $\text{Fe}_3\text{Al}$ , which, according to the total energy calculations, does not exist in pure  $\text{Fe}_3\text{Al}$  alloy. These results are in agreement with experimental findings, which indicate that in  $\text{Fe}_{2.8}\text{Mn}_{0.2}\text{Al}$  alloy, 12.55% of aluminium occupy B sublattice, whereas the remaining Al atoms are located at D positions [20]. If B–D type disorder is not taken into account for the configuration with Mn in (A,C) position, the total energy increases by 5 mRy/atom in comparison with the minimal total energy.

Shifting Mn atom to B site causes an increase of total energy by at least 57 mRy/atom in reference to the minimum total energy, independently of disorder's type. Analysis of total energies of different atomic configurations indicates that the disorder between (A,C) and D sublattices is unlikely. If one Al atom in supercell locates at (A,C) site, total energy increases by at least 23 mRy/atom with Mn atom in (A,C) position and by as much as 90 mRy/atom when Mn occupies B sublattice.

Assumed B–D-type disorder leads to a small decrease of total magnetic moment with respect to the total magnetic moment of totally ordered alloy. Moreover, this disorder does not lead to essential changes of Fe(A,C) magnetic moment because, in average, does not change the

composition of the first coordination sphere (both B and D positions constitute first coordination sphere, therefore B–D-type of disorder changes only spatial configuration of the Fe(A,C) environment, but does not change average number of Fe and Al atoms in the nearest environment).

Magnetic moment of Fe(D) is higher by about  $0.1 \mu_B$  than the magnetic moment of Fe(B). This is caused by higher average magnetic moment of the second coordination sphere of Fe(D) than of Fe(B).

Magnetic moments of manganese in both crystallographic positions exhibit similar values, in the range from  $2.14 \mu_B$  to  $2.39 \mu_B$ . However, depending on the position, the orientation of Mn magnetic moment is different. When manganese atom is located in B sublattice, its magnetic moment is oriented parallel to Fe moment. If Mn atoms occupy (A,C) positions, they exhibit antiparallel orientation with respect to the total magnetic moment.

Small negative magnetic moment is induced on aluminium atoms. Its value depends on the average magnetic moment of the local environment.

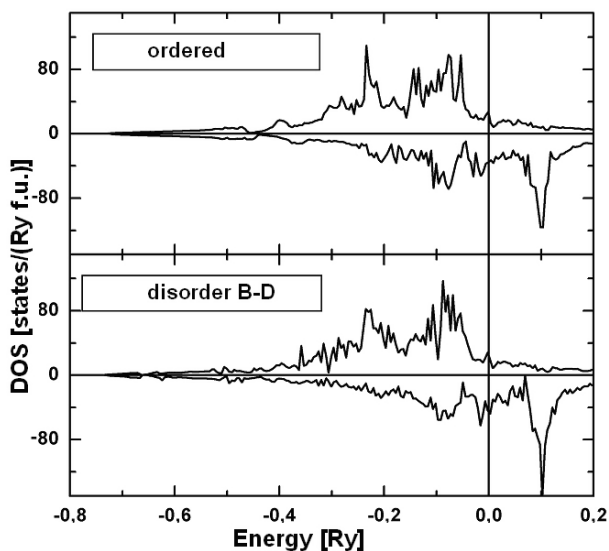


Fig. 2. Total density of states in Fe<sub>2.875</sub>Mn<sub>0.125</sub>Al with Mn in (A,C) position for ordered and partially B–D-type disordered atomic configurations.

Small disorder of B–D type in Fe<sub>2.875</sub>Mn<sub>0.125</sub>Al changes total densities of states (Fig. 2). Density of occupied low energy states (below  $-0.3$  Ry) diminishes whereas the DOS for higher energy ( $-0.15$  Ry) states increases. Furthermore, new states in minority subband above the Fermi energy appear. Narrow energy gap for energy about  $-0.65$  Ry, which has been found in Fe<sub>3</sub>Al, where B–D, or (A,C)–D type disordered was present, is also obtained when Fe is substituted by Mn (Fig. 2).

## 6. Summary

According to the total energy calculations Fe<sub>3</sub>Al compound should be fully ordered. Doping Fe<sub>3</sub>Al with transition metal may change ordering. In the case of chromium

( $x = 0.125$ ) impurity, the total energy difference between ordered and disordered states diminishes from 9 mRy/atom (for Fe<sub>3</sub>Al) to 1 mRy/atom (for Fe<sub>2.875</sub>Cr<sub>0.125</sub>Al). Nonetheless, the ordered state is still energetically preferred. Manganese doping Fe<sub>3</sub>Al locates preferentially in the parent compound — minimal total energy was obtained for the atomic configuration with 12.5% of aluminium located in B sublattice. This result is in agreement with experimental findings [20].

Magnetic moments of Fe(D) are higher than magnetic moments of Fe(B), which is connected with different atomic content of the third coordination sphere. For all considered atomic configurations, presence of B–D or (A,C)–D type of disorder leads to energy gap formation in the low energy region (about  $-0.65$  Ry).

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