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# *Ab initio* study of ordering degree in $Fe_3Si$ doped with Mn[*]

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Energetic stability of atomic exchange of sites between different sublattices in $Fe_3Si$, pure and doped with Mn, crystallizing in the $DO_3$-type structure is studied by *ab initio* calculations. A small chemical disorder between B and D sites preferred in $Fe_3Si$ and $Fe_{2.875}Mn_{0.125}Si$ is in good agreement with the Mössbauer studies.

Key words: *iron alloy; electronic structure; disordered alloy; local magnetic moment*

## 1. Introduction

$Fe_3Si$ alloy doped with 3d transition metals (Mn and Cr) has been investigated by *ab initio* calculations [1–3]. The object of the present study is $Fe_3Si$ which has the $DO_3$-type structure. In this structure, there are two nonequivalent sublattices (A, C) and B, which are occupied by Fe atoms, whereas all D sites are taken by Si. However, some Mössbauer measurements indicate that a small disorder exists between B and D sites [4, 5]. This means that some Si atoms occupy B sites and small fraction of Fe is also located at D sites.

In $Fe_{3-x}Mn_xSi$ alloy, Mössbauer measurements indicated an additional partial disorder between (A, C) and D sites [6]. Because of some discrepancies between theoretical and experimental results, it is attractive to go a little further and perform calculations in which experimentally found disorder would be taken into account.

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## 2. Details of calculations

Electronic structures of $Fe_3Si$ and $Fe_{2.875}Mn_{0.125}Si$ have been studied within the framework of the local spin-density approximation, using the self-consistent spin-polarized tight-binding linear muffin–tin orbital method in the atomic sphere approximation [7]. The exchange correlation potential was taken like in [1] with the non-local exchange correlation correction [8]. Similar to [1] the supercell with 32 atoms was used here. The calculations were carried out for ordered structure (all Si occupied only D sites) as well as for disordered ones in which one of Si atom occupied either B or (A, C) sites and thereby one of Fe atoms was located at D site. Mn impurity atom was allowed to occupy only B or (A, C) sites. Experimental values of lattice constants were used [9].

## 3. Results and discussion

### 3.1. Properties of $Fe_3Si$

We studied electronic structure of $Fe_3Si$ assuming three different arrangements of atoms in the supercell: Fe atoms are located at (A, C) and B sites only (1); "disorder B–D": one of the Si atom occupies B site and one of the Fe atoms locates at D site (2); "disorder (A, C)–D": B sites are occupied by Fe only, one of D sites is occupied by Fe atom, other D sites are occupied by Si, and one of (A, C) position is occupied by Si atom (3). Table 1 shows the results of total energy calculations. Our calculations confirmed experimental findings that small disorder between B and D sublattices may occur in $Fe_3Si$.

Table 1. Difference between total energy of the considered configuration and minimum total energy ($\Delta E$ [mRy/atom]); total [$\mu_B$/f.u.]) and local magnetic moments [$\mu_B$/atom] in $Fe_3Si$

| $Fe_3Si$ | ΔE | $\mu_{total}$ | $\mu_{Fe(A, C)}$ | $\mu_{Fe(B)}$ | $\mu_{Fe(D)}$ | $\mu_{Si(D)}$ | $\mu_{Si(B)}$ | $\mu_{Si(A, C)}$ |
|---|---|---|---|---|---|---|---|---|
| Ordered | 5 | 5.34 | 1.42 | 2.62 | – | –0.12 | – | – |
| Disorder B–D | 0 | 5.27 | 1.39 | 2.61 | 2.66 | –0.13 | –0.11 | – |
| Disorder (A, C)–D | 78 | 5.81 | 1.66 | 2.47 | 2.57 | –0.11 | – | –0.09 |

Minimum of the total energy was obtained for the supercell arrangement, where one Si atom is located in B site and thereby one Fe atom occupies D site. Such a disorder causes a decrease of total energy by 5 mRy/atom in comparison with the ordered structure. (A, C)–D disorder is energetically unprofitable and causes an increase of total energy by at least 78 mRy/atom. In B–D disordered state the total magnetic moment diminishes to $5.27\mu_B$ which is closer to the experimental value [10] than the total moment calculated for perfectly ordered phase. Furthermore, values of moments are generally slightly lower than in the ordered state. A small negative magnetic moment is induced on Si atom as postulated earlier in [5, 11]. Magnetic moment of Si(A, C) is lower than that of Si(B). This is connected with a smaller average magnetic moment of local environment of (A, C) site than the one of B site.

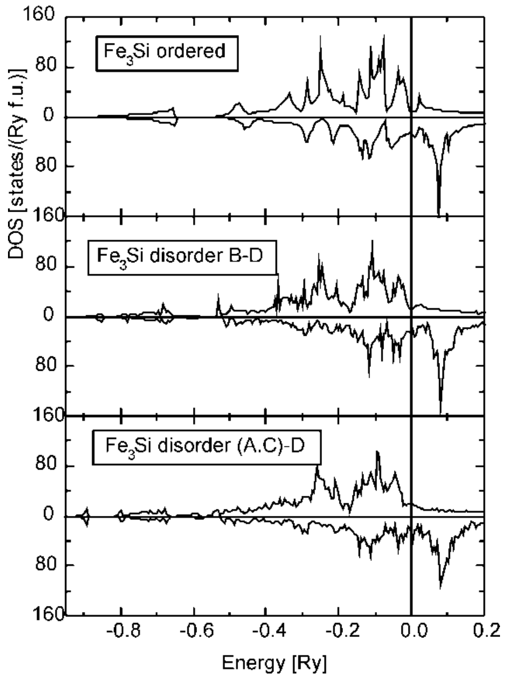

Fig. 1. The spin-projected total densities of states for $Fe_3Si$ in ordered, B–D and (A, C)–D disordered configurations

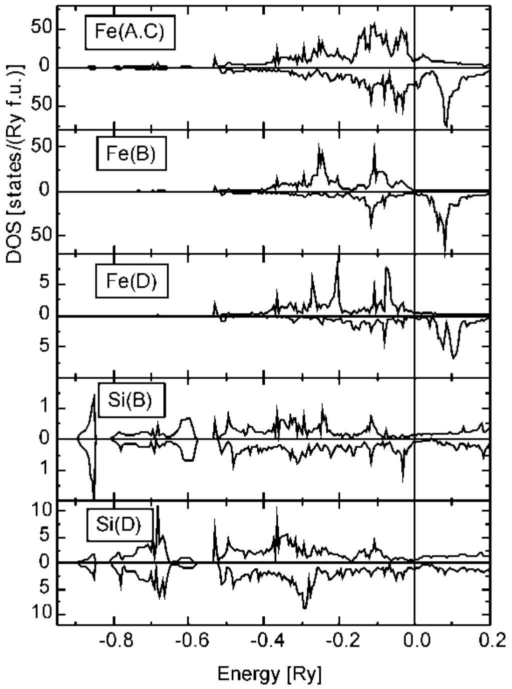

Fig. 2. The spin-projected local densities of states for $Fe_3Si$ in B–D disordered configuration

Total densities of states (DOS) in $Fe_3Si$ for three different arrangements of the supercell are presented in Fig. 1. The Fermi level (FL) is taken as the origin of the energy axis. In the perfectly ordered phase, the DOS is divided into two parts. The lower part (below –0.64 Ry) is mainly built by 3s states of Si with a small admixture of s, p states of Fe. In the upper part (above –0.53 Ry) 3d states of Fe overlap with 3p Si states. In region between –0.81 Ry and –0.57 Ry s and p states overlap. Above –0.54 Ry the total DOS is predominantly built of 3d states of Fe. The two gaps in the DOS of $Fe_3Si$, also visible at the (A, C)–D type of disorder (Fig. 1), are shifted towards lower energy region ([–0.88 Ry; –0.82 Ry], [–0.65 Ry; –0.64 Ry]). The disorder causes a decrease of the maximum peak in minority subband above FL thereby reducing a number of hole states in this energy range.

Figure 2 presents the DOS of Fe and Si atoms occupying different crystallographic positions in $Fe_3Si$ with B–D type disordered case. The shape of the DOS of Fe(B) is similar to DOS of *bcc* iron [12] because of the same nearest neighbour shell. Although Fe(D) has the same first nearest neighbours as Fe(B), its DOS differs because their second and third shells are different. However, the magnetic moment of Fe(D) is only slightly higher than the Fe(B) moment. Below the FL two main peaks in majority subband of Fe(D) exhibit pronounced splitting caused by crystal field. In the case of Fe(D) its d orbitals are more strongly affected than d orbitals of Fe(B). The additional crystal field splitting occurs in the DOS of Fe(D) when the orbitals are located in a region of high electron density. The nearest neighbourhood of Fe(A, C) in $Fe_3Si$ is formed by Fe and Si atoms. This is reflected in a much more complex DOS. For higher energies (above –0.54 Ry), the densities of states of Si(B) and Si(D) show similar shape formed mainly by p states but for s states (below –0.57 Ry) strong differences are visible. It is observed that s states of Si(B) are shifted towards lower energies.

### 3.2. Properties of $Fe_{2.875}Mn_{0.125}Si$

The results of calculations for $Fe_{2.875}Mn_{0.125}Si$ are summarized in Table 2. The lowest energy is obtained for the atomic configuration where Mn occupies B site and a small disorder between B and D sublattices exists. All other investigated configurations have total energies higher by at least 8 mRy/atom. Position exchange of Fe and Si causes a decrease of total magnetic moment with respect to the ordered phase. This may explain the experimentally observed situation [13]. B–D disorder causes simultaneously a slight increase of Fe(B) moment and a decrease of Fe(A, C) moment. The calculations show that the spin of Mn(A, C) surrounded by 5 Fe and 3 Si atoms would reverse in (A, C)–D disordered case. Migration of Si to the B site causes an increase of the absolute value of its local moment to $-0.16\mu_B$ whereas Si(A, C) has 25% smaller spin polarisation than Si(D). For all considered atomic arrangements of the supercell, Si(D) has a small moment ($-0.12\mu_B$).

Table 2. The difference between total energy of the considered configuration and minimum total energy ($\Delta E$ [mRy/atom]); the total [$\mu_B$ /f.u.]) and local magnetic moments [$\mu_B$/atom] in $Fe_{2.875}Mn_{0.125}Si$

| $Fe_{2.875}Mn_{0.125}Si$ | | $\Delta E$ | $\mu_{total}$ | $\mu_{Fe(A, C)}$ | $\mu_{Fe(B)}$ | $\mu_{Fe(D)}$ | $\mu_{Mn}$ | $\mu_{Si(D)}$ | $\mu_{Si(B)}$ | $\mu_{Si(A, C)}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Mn (B) | ordered | 8 mRy | 5.25 | 1.38 | 2.61 | – | 2.53 | –0.12 | – | – |
| | disorder B–D | 0 | 5.17 | 1.35 | 2.63 | 2.65 | 2.44 | –0.12 | –0.16 | – |
| | disorder (A, C)–D | 74 mRy | 5.67 | 1.59 | 2.50 | 2.56 | 2.31 | –0.12 | – | –0.09 |
| Mn (A, C) | ordered | 29 mRy | 5.39 | 1.45 | 2.60 | – | 1.50 | –0.12 | – | – |
| | disorder B–D | 17 mRy | 5.29 | 1.40 | 2.60 | 2.59 | 1.60 | –0.12 | –0.16 | – |
| | disorder (A, C)–D | 23 mRy | 5.32 | 1.61 | 2.45 | 2.51 | –1.35 | –0.10 | – | –0.09 |

# 4. Conclusions

*Ab initio* studies of total energy indicate possibility of a B–D disorder in $Fe_3Si$. This explains why in the Mössbauer studies of $Fe_3Si$ [4], a hyperfine field on Fe(D) is observed. The magnetic moments of Fe(B) and Fe(D) turn out to be not much different. Doping parent $Fe_3Si$ with Mn does not change ordering. In the most likely structure of $Fe_3Si$ with B–D type disordering, the low-energy s band splits into two bands. Considered disorder between D and other sublattices turns out not to change substantially neither total nor local magnetic moments.

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