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Electronic structure and magnetism of $Fe_3Al_{1-x}Si_x$ alloys

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ABSTRACT

Total energy and electronic structure calculations for $Fe_3Al_{1-x}Si_x$ alloys with DO_3-type structure have been performed to understand structural and magnetic properties using plane-wave pseudopotential method. With the increase of Si content, the equilibrium lattice constants reduce linearly and the saturation magnetic moments per unit cell of $Fe_3Al_{1-x}Si_x$ alloys decrease, which are in good agreement with the experimental results. To illustrate the origin of magnetism of $Fe_3Al_{1-x}Si_x$ alloys, spin-polarized density of states and local magnetic moments are investigated. The results show that the difference in local moments of Fe(A,C) and Fe(B) is due to different local environment in DO_3-type structure and the relative affinity of Si and Al for Fe. In addition, to analyze the effect of Si on the magnetism of Fe_3Al, the Mulliken charge and bond population are used to study the charge transfer and the bonding types, respectively. The calculated results give a reasonable explanation of recent experimental findings.

1. Introduction

Fe_3Si and Fe_3Al alloys have excellent soft magnetic properties and they are used as motor and transformer cores. The relationship between structural and magnetic properties in Fe-based magnetic systems has been extensively studied [1–5]. It is interesting to note that the DO_3 ordering is rather easily achieved in the Fe_3Si alloy, whereas it is extremely difficult to order Fe_3Al alloy fully [6]. Intuitively, the two isomorphous alloys should show very similar properties. However, their mechanical properties are of striking difference. Fe_3Si is brittle, whereas Fe_3Al is ductile. In order to improve their mechanical and magnetic properties, researchers mixed the two binary alloys into FeAlSi ternary alloy, for example, an almost 2: 3 mixture of these two alloys, called Sendust, or introduces Si ions into FeAl alloys [1].

In fact, important changes take place in the structural properties as well as in the magnetism when Al is substituted by Si. Legarra et al. [7] found that Si substitution prevents the disordering of the alloys. According to the experimental data [8–10], the FeAlSi alloys crystallize in the DO_3-type structure. Additionally, Si and Al atoms preferentially occupy D positions in the all range of studied concentration. There are two non-equivalent Fe sites [(A, C) and B] with different nearest neighbor (NN) configurations in the perfectly ordered structure. As a consequence of different nearest environments of atoms at these sites different electronic and magnetic properties connected with these positions are observed [3]. In Fe_3Si compound, magnetic moment of Fe at B site is reported to be within the range of 2.20 μ_B [11] to 2.44 μ_B [12]. These values are close to the magnetic moment of Fe in bcc structure. Since the Fe atom at (A, C) site has fewer NN Fe atoms, its magnetic moment is smaller too, and within the range of 1.18 μ_B [12] to 1.35 μ_B [11]. Magnetic properties of $Fe_3Al_{1-x}Si_x$ alloys are quite complex. Recently, a decrease of the magnetic moment of Fe with the Si content is clearly observed by Mössbauer measurements [7,13]. However, the experimental and theoretical [14–16] values do not agree well.

The aim of the present work is to assess intrinsic properties of magnetically ordered $Fe_3Al_{1-x}Si_x$ alloys and the effect of Si substitution for Al at the cube D sites within $Fe_3Al_{1-x}Si_x$ ordered alloys. The paper is organized as follows. Section 2 describes some technical details about the model and methodology applied. Section 3 reports and discusses the results. Section 4 draws some conclusions.

2. Calculation model and methods

The system under study has DO_3-type crystal structure, as shown in Fig. 1, which is composed of four interpenetrating fcc lattices shifted by 1/4th of the main diagonal. These sublattices are abbreviated as A, B, C and D and originated at (0, 0, 0), (1/2, 1/2, 1/2), (1/4, 1/4, 1/4), (3/4, 3/4, 3/4). The A and C sublattices are symmetry equivalent in DO_3-type structure. In ideal Fe_3Al alloy with DO_3-type structure, Fe atoms occupy two non-equivalent sites (A, C) and B, while D-sites are occupied by Al atoms. Here, the substitution of Si for Al at D positions is considered at the composition x: 0, 0.25, 0.50, 0.75, 1.00. We find it interesting to investigate electronic structure

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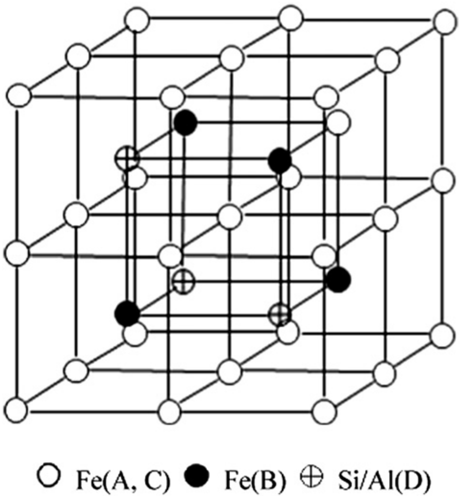

Fig. 1. The unit cell of DO_3 crystal structure. The B and (A, C) sites are occupied by Fe. The D sites are occupied by Si and Al.

and intrinsic magnetic properties of $Fe_3Al_{1-x}Si_x$ ordered alloys, paying special attention on the concentration range.

First-principles calculations were performed in the framework of density functional theory within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof [17] exchange correlation potential, and utilizing the plane-wave total energy pseudopotential method as implemented in CASTEP code [17,18]. The ion–electron interaction is modeled by ultrasoft pseudopential in the Vanderbilt form [19]. Using these methods, satisfactory results have been received in other studies [20,21]. The valence atomic configurations are $3d^64s^2$ for Fe, $3s^23p^1$ for Al and $3s^23p^2$ for Si atom. For the 16-atom unit-cell calculations, the cutoff energy of plane waves was set to 380 eV and a k-point mesh $7 \times 7 \times 7$ was used. Geometry optimizations were performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method [22]. Atomic relaxations were considered to be converged when the residual forces were smaller than 0.01 eV/Å. For all the relaxed structures, the Mulliken charges and bond populations were investigated using a projection of the plane wave states onto a linear combination of atomic orbitals (LCAO) basis set [23,24], which is widely used to perform charge transfers and populations analysis.

3. Results and discussion

We started the geometry optimization of Fe_3Al structure with a lattice constant from experiment: a = 5.793 Å [8]. The calculations were carried out for both spin-polarized (SP) and non-spin-polarized (NSP) configurations. The DO_3 structures have equilibrium lattice constants: $a_{SP}(Fe_3Al) = 5.736$ Å, $a_{NSP}(Fe_3Al) = 5.608$ Å, with an energy difference of $\Delta E_{(SP\text{-}NSP)} = -3.404$ eV per unit cell favoring the SP configuration. Moreover, calculated lattice constant of Fe_3Al for SP configuration is only 0.98% smaller than the experimental value [8]. To examine the effect of Si on the structure and magnetization of Fe_3Al, the structures of $Fe_3Al_{1-x}Si_x$ for SP and NSP configurations were also studied. Fig. 2 shows that the energy difference of $\Delta E_{(SP\text{-}NSP)}$ is negative on all the range x, indicating that the ferromagnetic state (FM) is largely energetically preferred over the nonmagnetic one. ΔE for Fe_3Si has the lowest value, which suggests the strong magnetic coupling interaction between Fe atoms in Fe_3Si.

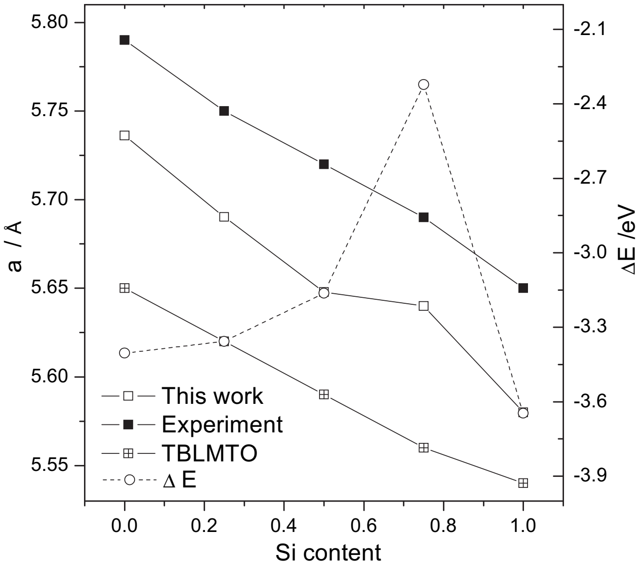

Fig. 2. Lattice parameter (left) and ΔE (right) versus Si content for ordered $Fe_3Al_{1-x}Si_x$ sample series. The experimental values and the theoretical results from TBLMTO method are taken from Ref. [8] and [25], respectively.

Lattice constants corresponding to the DO_3 unit cell at all composition x are shown in Fig. 2. Due to the Si insertion in the D site of Fe_3Al, the volume shrinkage is about 2.6% at x = 1.00, which is smaller than the experimental value of 5.653 Å [8]. The lattice constants decrease with Si content. Assuming a linear dependence of the lattice parameter a on x, we have found that

$$a = 5.735 - 0.142x \tag{1}$$

Lattice parameter inferred from Eq. (1) for x = 0.750 and x = 0.875 agrees excellent with the published value for $Fe_3Al_{0.25}Si_{0.75}$: 5.688 Å [7,13], and for $Fe_3Al_{0.125}Si_{0.875}$: 5.670 Å [7,13], which excel the theoretical result from TBLMTO method [25]. The results show that the Fe–Fe distances in this alloys decrease from 2.48 to 2.42 Å when Si content increases. However, the Fe–Al and Fe–Si distances are 2.48 and 2.42 Å, respectively, which hardly vary with Si content. The volume shrinks, as shown in Table 1, referring the decrease of the Fe–Fe distance. And bulk modulus slightly increases when the Si content increases, which implies that the interaction of Fe–Si bond is stronger than that of the Fe–Al bond. With the exception of Fe_3Si, Si atoms substitute for Al in lattice the cubic environment of Fe sites become somewhat distorted [9], which is identified by the calculated values of bond length, as shown in Table 2.

The SP electronic energy bands of the $Fe_3Al_{1-x}Si_x$ compounds are investigated to compare the exchange interaction. The bands corresponding to the spin-up (↑) and spin-down (↓) electrons split apart are due to the exchange coupling between the electrons. In fact, exchange splitting Δ_x reflects the strength of exchange interaction between the magnetic ions. In the present case the 108 bands near Fermi level are considered. The statistical average of exchange splitting is obtained from the band calculation, which is the result of self-consistent field calculations. The statistical average values of exchange splitting$\Delta_X = E_{i\uparrow} - E_{i\downarrow}$ are negative (as shown in Table 1). The Curie temperature of the binary compound consisting of magnetic ions i and j can be expressed as $T_c = Z(n_i^2 J_{ii} + n_j^2 J_{jj} + 2n_i n_j J_{ij})/2k$, which had been described in ref. [26]. Here, ions i and j are Fe(A,C) and Fe(B), respectively. Because the Si and Al atoms are slightly SP, as shown in Table 1, the expression can be approximately used for the $Fe_3Al_{1-x}Si_x$ compounds. According to the