A First-principles Study on Magnetism of Al Impurity in bcc Fe

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The magnetism and electronic structure of bcc Al₁Fe₂₆ was investigated by means of first-principles calculations with and without spin-orbit coupling (SOC). From the calculated total energy, the SOC corrected system is shown to be approximately 5 meV per atom lower than the SOC uncorrected system. The induced spin magnetic moment at the Al site was −0.125 µB without SOC and −0.124 µB with SOC. The orbital magnetic moments were calculated to be 0.002 µB in [100] direction for Al. The electronic structures showed the nearest neighbor antiferromagnetic interaction between Fe and Al to be essential for determining the magnetism of the Al₁Fe₂₆ system.

Keywords: Fe, Al impurity, magnetism, spin-orbit coupling, first-principles

1. Introduction

An iron-aluminum system in its Fe-rich portion is interesting given its complex magnetic phase diagram and order-disorder transformation. Alloys based on the Fe-Al intermetallic phases matrix are becoming increasingly popular in terms of practical usage due to their high resistance to oxidation, carbonization, and sulfurization processes at high temperatures and their resistance to the effects of exposition to liquid salts [1]. Another important factor deciding application is the low cost of their main components, iron and aluminum. A high content of aluminum also lowers the intrinsic alloy density, which correspondingly lowers the weight of the components constituting the alloy [1-3].

However, high Al contents can create many side effects on steel (complicated Fe-Al compounds, Fe-Al-C compounds, i.e., κ-carbide), which greatly affect the creep properties or deformation mechanics. These technological problems have thus been discussed in the literature. It is also well known that Al is a ferrite former through destabilization of the austenite domain. Contrary to the 3d alloying elements in bcc Fe [4], the group III-VI elements show strong spin-orbit coupling (SOC) effects, especially upon magnetism, Si in bcc Fe [5]. Newly developed lightweight steels based on ferritic iron aluminum alloys show promising physical, mechanical, and technological properties such as high specific elastic stiffness and strength, excellent ductility and formability, reduced specific weight, and an improved corrosion resistance. However, the environmental embrittlement at room temperature regions [6] has not been solved yet.

Instead of addressing the room temperature ductility of Fe-Al intermetallic phases, new functional properties of the Fe-Al system, its relatively high magnetostriiction near 20 at% aluminum contents, has been considered [7, 8]. The observed high magnetostriiction is considered to be responsible for the transition from a disordered to an ordered phase by increasing aluminum contents. However, the effects of the intrinsic magnetic properties on the dilute alloying region are seldom considered. As such, it is essential to study the effects of Al on the electronic structure and magnetism of bcc Fe, important not only from an applications point of view, but also from a fundamental understanding point of view. Here, we not only investigate the electronic and magnetic properties of bcc Fe-Al, but also the effects of SOC on bcc Fe-Al magnetism.

2. Computational Method

A 3×3×3 supercell of bcc Fe, corresponding to 27 Fe atoms within the unit cell, was considered for Al sub-

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2. Methodology

The computational method employed in this study is the full potential linearized augmented plane wave (FLAPW) [9, 10] method under the generalized gradient approximation (GGA) [11]. An energy cutoff of 4.0 \((2\pi/a)\), where \(a\) is the lattice parameter of each calculation, was employed for expanding the linearized augmented plane wave (LAPW) basis set. This plane wave cutoff corresponds to \(2350\) LAPWs per \(k\)-point and spin. A \(16.1245\) \((2\pi/a)\) cutoff was used for the star functions depicting the charge density and potential in the interstitial regions. Lattice harmonics with \(l \leq 8\) were employed to expand the charge density, potential, and wave functions inside each muffin-tin (MT) sphere, with a radius of \(2.2\) a.u. for all the atoms. Integrations inside the Brillouin zone (BZ) were performed using the improved tetrahedron method [12] over a \(13 \times 13 \times 13\) mesh within the three-dimensional 3D-BZ, corresponding to 84 \(k\)-points inside the irreducible wedge of the 3D-BZ.

All core electrons were first treated fully relativistically and valence states scalar relativistically, without spin-orbit coupling (SOC) [13]. For spin-orbit coupling on valence states, we then employed the second variation method [14] with the spin diagonal parts of the density subjected to a self-consistency loop. During the second variation procedure, integrations inside the 3D-BZ were executed in the full-BZ, the \(1099\) \(k\)-points. The explicit orthogonalization (XO) scheme was employed to ensure the orthogonality between the core and valence states [15].

All atoms were fully relaxed at each lattice volume until the atomic forces on each atom were less than \(2\) mRy/a.u. The selected computational parameters fulfilled the convergence criterion [16]. The equilibrium lattice constants and bulk moduli \(B\) were determined by the fifteen-point fitting of the total energy and volume to the Birch-Murnaghan equation of states [17]. Using the optimized lattice constants, further calculations were carried out with and without SOC.

3. Results and Discussions

Calculations were carried out in the nonmagnetic (NM) and ferromagnetic (FM) states, with the total energy calculations indicating the FM state to be more stable than the NM state at the optimized lattice constant. Considering the effects of the SOC, the authors observed that the FM state with SOC to be approximately \(5\) meV per atom lower than the FM state without SOC. Accordingly, we will focus only on the FM state with and without SOC, and the attention will not be given to the NM and FM states without structural relaxation as they were higher in energy.

The lattice parameters of the bcc \(\text{Al}_1\text{Fe}_{26}\) were optimized and the calculated lattice parameter was \(8.513\) Å without SOC or atomic relaxation. However, this value changed to \(8.510\) Å when the atomic relaxation was allowed, indicating that the atomic relaxation slightly changed the volume of the unit cell. The approximately same value \((8.510\) Å\) was obtained upon repeating the calculations with SOC and atomic relaxation. Therefore, SOC does not bear any significant effect upon the \(\text{Al}_1\text{Fe}_{26}\) lattice constant. From the equation of state [17], we also estimated the bulk modulus \(B\) to be \(175.41\) GPa without SOC, and when the SOC was allowed, \(B\) was calculated to be \(175.95\) GPa. This shows that the solid solution hardening is not as significant at this Al content compared to that \((175.75\) GPa\) of the pure bcc Fe [4].

The calculated magnetic moments within the MT sphere
are shown in Table 1. It is clear that the induced magnetic moment at Al is negative, showing that the Fe-Al couples antiferromagnetically. It is interesting that the effects of the SOC is not so significant. Although Al decreases the Fe₁ magnetic moment, the magnetic moments of Fe₂ and Fe₃ are the same with the pure bcc Fe value (~2.23 \( \mu_B \)) at the optimized lattice constant [4]. This suggests that the effects of the Al impurity are well screened within the nearest neighbor. Note that the similar behavior was also discovered in the bcc Ni₁Fe₂₆ system [18]. We thus conclude that the first nearest neighbor magnetic interactions are playing a vital role in the magnetism of bcc Fe, and depending on the impurity atoms, the magnetic moment of Fe₁ can be increased or decreased [4, 6, 18, 19].

To further demonstrate the effects of SOC on the magnetism of Al₁Fe₂₆, the orbital magnetic moments of the Al, Fe₁, Fe₂, and Fe₃ atoms are shown in Table 2. For comparison purposes, the unrelaxed and relaxed values of the magnetic moments are shown. One can see that atomic relaxation has only an effect on the Fe₁ atoms. In the unrelaxed case, the orbital magnetic moments of Fe₁ are in the [\(1\ 1\ 1\)] direction, whereas in the relaxed case, these are directed in the [\(1\ 1\ 0\)] direction. It is of imperative note that the orbital magnetic moments direction of the Fe₁ is similar to pure bcc Fe [19]. It is also important to note [19] that the orbital magnetic moments of the Fe₁ atoms in the bcc Si₁Fe₂₆ and Al₁Fe₂₆ are directed in the

Table 1. Calculated spin magnetic moments in units of \(\mu_B\) inside each muffin-tin (MT) sphere of Al₁Fe₂₆ with spin-orbit coupling (SOC) and without SOC cases.

<table>
<thead>
<tr>
<th>Case</th>
<th>Al</th>
<th>Fe₁</th>
<th>Fe₂</th>
<th>Fe₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>With SOC</td>
<td>-0.124</td>
<td>2.110</td>
<td>2.224</td>
<td>2.223</td>
</tr>
<tr>
<td>Without SOC</td>
<td>-0.125</td>
<td>2.112</td>
<td>2.227</td>
<td>2.226</td>
</tr>
</tbody>
</table>

Table 2. Calculated orbital magnetic moments with SOC in units of \(\mu_B\) inside each muffin-tin (MT) sphere of: (a) unrelaxed; (b) relaxed Al₁Fe₂₆.

(a)

<table>
<thead>
<tr>
<th>Atom</th>
<th>(L_x)</th>
<th>(L_y)</th>
<th>(L_z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>-0.003</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe₁</td>
<td>-0.013</td>
<td>0.013</td>
<td>-0.001</td>
</tr>
<tr>
<td>Fe₂</td>
<td>0.014</td>
<td>0.016</td>
<td>0.014</td>
</tr>
<tr>
<td>Fe₃</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.016</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th>Atom</th>
<th>(L_x)</th>
<th>(L_y)</th>
<th>(L_z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>-0.002</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe₁</td>
<td>-0.012</td>
<td>0.012</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe₂</td>
<td>0.014</td>
<td>0.016</td>
<td>0.014</td>
</tr>
<tr>
<td>Fe₃</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.016</td>
</tr>
</tbody>
</table>

Fig. 2. Calculated orbital projected density of states (DOS) of Al₁Fe₂₆, the orbital magnetic moments of the Al, Fe₁, Fe₂, and Fe₃ atoms with spin-orbit coupling (SOC). The DOS values of the \(p\) states are multiplied by a factor of 20. The upper and lower panel shows spin-up and spin-down states, respectively. The Fermi level (\(E_F\)) was set to zero. The solid and broken lines represent the \(t_{2g}\) and \(e_{g}\) states of Fe.
same direction, [1 10]. Though the orbital magnetic moments are directed in the same direction in the Al₁Fe₂₆ and Si₁Fe₂₆, the magnitude of the orbital magnetic moment of Fe₁ is different for signifying the different hybridization between the Al₁Fe₂₆ and Si₁Fe₂₆.

To see the Fe₁-Al interactions thoroughly, we present the electronic density of states (DOS) of the Al₁Fe₂₆ in Fig. 2, where the solid and broken lines represent \( t_{2g} \) and \( e_g \) states of the Fe atoms, respectively. The Fermi level \( E_F \) was set to zero. The \( d \) states of the Fe are decomposed into \( e_g \) and \( t_{2g} \) states. One can easily see strong hybridization between the Fe₁ and Al atoms; this strong hybridization of Fe₁ with Al causes reduction of the magnetic moment of Fe₁ compared with Fe₂ and Fe₃. Near \( E_F \), the Fe₁ \( t_{2g} \) and Al \( p \) bonding is dominated in the minority spins where one can see a small peak at Fe₁, just below \( E_F \). The majority spin DOS of \( t_{2g} \) at \( E_F \) is flat for the Fe₂ and Fe₃ atoms. However, the electronic density of \( t_{2g} \) decays rapidly and delocalizes the \( t_{2g} \) electrons due to the covalent nature of Fe₁-\( t_{2g} \) and Al-\( p \) orbitals at \( E_F \). The Fe₂ and Fe₃ atoms are far from the Al atoms and do not strongly interact with the Al atoms; the DOS of Fe₂ and Fe₃ are similar to pure bcc Fe [4]. Further determination of the spin density contours would give an idea about the nature of magnetic coupling between the magnetic elements. The spin density contour corrected with SOC in the (110) plane of the Al₁Fe₂₆ is shown in Fig. 3. This figure shows that the induced magnetic moment at Al is negative, represented by dashed lines. The Fe₁ and Al atoms couple antiferromagnetically with each other, consistent with the local magnetic moments within the MT spheres. The antiferromagnetic interactions of Fe₁ with Al decrease the local magnetic moment of the Fe₁, compared with Fe₂ and Fe₃. The Fe₂ and Fe₃ atoms also interact antiferromagnetically with Al, but this interaction is not sufficiently strong to decrease the local magnetic moment due to short-range nature of the antiferromagnetic coupling.

4. Summary

Using \( ab\text{-}initio \) calculations, the magnetic and electronic properties of 3.7 at% Al in bcc Fe were studied. We considered the effects of spin-orbit (SOC) coupling on the magnetism and electronic structures of Al₁Fe₂₆. The calculations herein showed that SOC did not change the magnetic moments at the Al and Fe sites. The electronic density of states showed a strong hybridization between the Fe₁ and Al atoms; this strong hybridization decreased the local magnetic moments of Fe₁. The spin density contours revealed that the Fe₁ and Al atoms interact antiferromagnetically and decrease the magnetic moment of the Fe₁ compared with Fe₂ and Fe₃.

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References