Ab initio study of the anomalous volume-composition dependence in Fe–Al alloys

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ABSTRACT

The experimentally observed anomalous compositional dependence of the lattice constant of Fe–Al crystals has been theoretically investigated employing density functional theory (DFT) within the generalized gradient approximation (GGA). The formation energies, equilibrium volumes and magnetic states have been determined for a dense set of different aluminium concentrations and a large variety of atomic configurations. The spin-polarized calculations for Fe-rich compounds reproduce very well the anomalous lattice-constant behavior in contrast to both the nonmagnetic and fixed-spin-moment calculations that result in nearly linear trends without any anomaly. We thus identify the change in magnetism of iron atoms as caused by an increasing number of Al atoms in the first coordination spheres to be the decisive driving force of the anomalous behavior.

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The development of new lightweight materials is crucial for numerous energy-conversion units or applications in automotive and aerospace industries. Low-cost low-density materials operating at higher temperatures ensure a lower fuel consumption or environmentally cleaner and more efficiently produced electricity. In order to invent new strategies in materials design of these materials, a comprehensive understanding of fundamental mechanisms in existing lightweight alloys has to be achieved. Two basic options in materials optimization are their chemical composition and structure. Both characteristics are mutually interlinked and inherently multi-scale in nature what make them challenging to study. We address these fundamental aspects for an important class of lightweight materials, iron-rich Fe–Al alloys.

Iron aluminides represent a promising class of intermetallics with great potential for substituting stainless steels at elevated and high temperatures. Noteworthy is their excellent chemical resistance with respect to corrosion and sulfidation processes [1], low cost of their constituents, high strength, and particularly density $(5700–6700 \text{ kg/m}^3)$ lower than that of steel (7850 kg/m^3). Previous attempts to further reduce the density in order to obtain even lighter materials have been hampered by the fact that the dependence of the volume, or equivalently the lattice constant, on the alloy composition is rather complex. In contrast to many alloys where the lattice constant changes nearly linearly as a function of composition, several experimental studies on Fe–Al alloys observed an anomalous behavior over large parts of the concentration range (see Fig. 1 a). A thorough overview of experimental studies performed until 1958 can be found in Ref. [2], for later studies see e.g. Refs. [3,4].

It has been observed in experiments that the lattice-constant dependence turned out to depend on the processing history of the samples. The influence of thermal and mechanical treatment may be seen from comparison of (i) the as cast and quenched and (ii) crushed samples in Fig. 1 a.

It has also been known from experiments that crucial features of the lattice-constant dependence nearly coincide with the three main phases within the Fe–Al phase-diagram, namely with (i) a disordered solid solution α, (ii) a phase based on the Fe3Al intermetallic in the D0₃ structure and finally (iii) the FeAl phase with B2 (CsCl-type) structure (see comparison of Fig. 1 a, b).

At low temperatures where the lattice constant measurements have been performed the phase diagram in Fig. 1 b shows the α-phase for the lowest Al-content (up to 18 at.% Al), the D0₃-based intermetallics for the concentration range from 18 to 37 at.% Al, and the B2-phase up to $\approx$ 49 at.% Al. Based on the above summarized experimental observations two mechanisms were suggested to explain the lattice-parameter deviation from the linear trend at Al-content above 18 at.%. The anomaly was tentatively assigned to either the onset of ordering, i.e., a disorder-order transition (see e.g., [4]), or it was speculated to be due to a magnetic transition in the Fe atoms (see e.g., [2]). In contrast to the ordering hypothesis, it was not possible to experimentally test the interpretation identifying
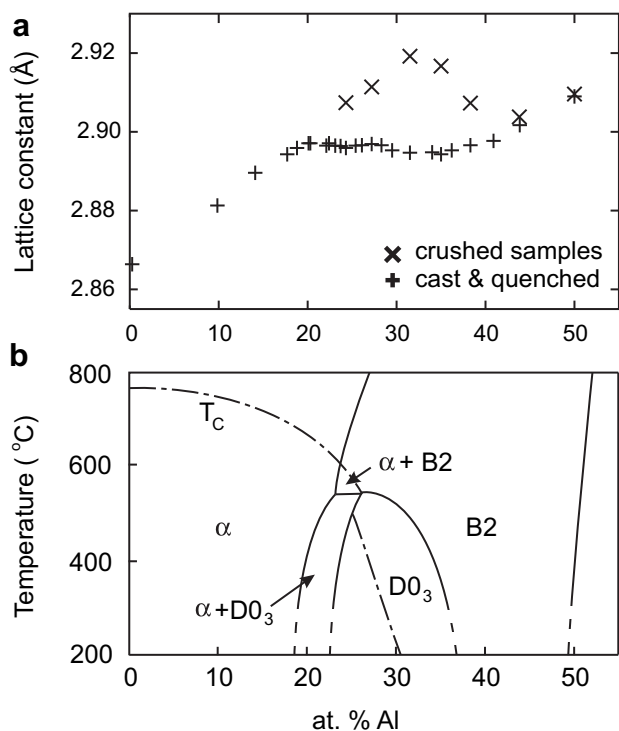
Fig. 1. Compositional dependence of the experimental lattice constants for the cast and crashed samples adapted from Taylor *et al* [2] (a). The data points are expected to have error bars under 0.0001 Å. Fig. b) shows simplified Fe-rich part of the Fe–Al phase diagram up to 800 °C with the Curie temperature concentration dependence T_C and three Fe–Al phases, a disordered solid solution α and ordered $D0_3$ and B2 structures (see the text). Dashed lines indicate the phase boundaries that are experimentally difficult to determine.

magnetism as the decisive driving force. In the present paper, we will therefore address this issue using theoretical calculations based on fundamental quantum mechanics applied to solids.

The binary Fe–Al alloys have been studied in a number of previous theoretical studies. Staunton *et al* [5] used a concentration-wave mean-field approach in order to study two high temperature transitions, the ferromagnetic–paramagnetic and the $D0_3$-B2 structural transition in $Fe_{80}Al_{20}$ solid solution. Lechermann et al. [6] performed density-functional-theory (DFT) total-energy calculations at zero temperature for Fe_3Al in the ordered $D0_3$ and $L1_2$ structures using both all-electron and pseudopotential methods. Based on these studies the Fe–Al system was identified as one of the most challenging for modern theoretical studies as DFT calculations reach their accuracy limit [7].

Further first-principles calculations focused on formation energies of bcc iron and fcc aluminum, B2 (FeAl), B32 (FeAl) and $D0_3$ (Fe_3Al and $FeAl_3$) compounds. These studies were performed by e.g. Gonzales-Ormeño et al. [8] within density functional theory (DFT) using the Full Potential – Linear Augmented Plane Wave method (FP-LAPW) and focused on both spin-polarized and spin non-polarized states. The calculated formation energies of both Fe_3Al and FeAl compounds showed excellent agreement with available calorimetric data. Using a different method (Tight Binding Linear Muffin-Tin Orbital), Apiñaniz et al. [9] calculated the magnetic and structural properties of ordered and disordered FeAl alloys [10, 11] or Si-containing compounds [12] and compared the results to experimental obtained findings. Systematically varying chemical compositions and the positions of Fe and Al atoms in a BCC superstructure, the total energy, bulk modulus, lattice parameter and magnetic moments were determined for B2, $D0_3$ and B32 ordered structures and A2 disordered structure. In

this way, the order–disorder transition in Fe–Al alloys was examined. The disordered states were found to exhibit both larger Fe magnetic moments and lattice parameter than the ordered ones.

Recently, an *ab initio* study by Lechermann et al. [13] focused on the Ni–Fe–Al ternary phase diagram combining two state-of-the-art methods, namely the cluster expansion method for a representation of the energy landscape at $T = 0$ K over the whole Gibbs triangle and the cluster variation method in the tetrahedron approximation to simulate finite-temperature effects. Similarly, through the combination of the full potential-linear augmented plane wave and cluster expansion method, the metastable phase diagram of the body-centered cubic-based ordering equilibria in the Fe–Al system has been calculated by Gonzales-Ormeño et al. [14] including the spin polarization of Fe in the thermodynamic model. In another paper by Gonzales-Ormeño et al. [15], the influence of the nearest neighborhood on the magnetic behavior at Fe sites in bcc-based Fe–Al, Fe–Mo, and Fe–Al–Mo alloys was studied.

The focus in all the previous studies has been more on specific structures/compositions. A detailed and systematic analysis of the anomaly is still lacking and will be the focus of the present paper.

Methodology

In order to determine compositional trends of (i) the formation energy, (ii) the lattice constant and/or (iii) magnetic moment, a dense set of local atomic configurations and Al-concentrations has been studied using the supercell approach. Due to the fact that all states of the iron-rich part of the Fe–Al phase diagram are related to the body-centered cubic structure (bcc), an identical supercell has been used in our calculations. The supercell consists of eight (2 x 2 x 2) elementary bcc unit cells with a 16-atomic basis (see fig. 2). The total number of atoms in the supercell determines the minimum concentration step. For the 16 atom cell considered here it is 1/16, i.e. the concentration steps are 6.25 at.%. When the supercell geometry allowed for more than one atomic configuration at a given concentration, the total energies and other characteristics have been calculated for a set of selected non-equivalent structures. Further details of the computed phases are summarized in the Table 1.
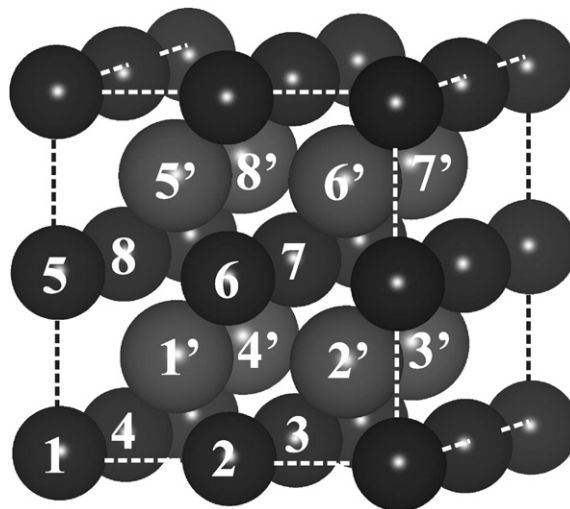

Fig. 2. The 2 x 2 x 2 16-atomic supercell used in the calculations with one half of the atoms (numbered 1–8) located in the corners of the elementary bcc cells and the second half (numbered 1′–8′) in the body-centered positions (for sake of clarity depicted by slightly larger spheres).