Structure and stability of Al$_2$Fe and Al$_5$Fe$_2$: First-principles total energy and phonon calculations

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We employ first-principles total energy and phonon calculations to address the structure and stability of Al$_2$Fe and Al$_5$Fe$_2$. The observed structure of Al$_2$Fe, which is reported as stable in the assessed Al-Fe phase diagram, is distinguished by an unusually low triclinic symmetry. The initial crystallographic structure determination additionally featured an unusual hole large enough to accommodate an additional atom. Our calculations indicate that the hole must be filled, but predict that the triclinic structure is unstable relative to a simpler tetragonal structure based on the prototype MoSi$_2$. This tetragonal structure is interesting because it is predicted to be nonmagnetic, electrically insulating, and high density, while the triclinic structure is magnetic, metallic, and low density. We reconcile this seeming contradiction by demonstrating a high vibrational entropy that explains why the triclinic structure is stable at high temperatures. Finally, we note that orthorhombic Al$_5$Fe$_2$ is also destabilized by the tetragonal structure but may be stabilized at high temperatures, again by vibrational entropy and partial occupancy associated with the diffusion of Al atoms along channels.

I. INTRODUCTION

Aluminum-based intermetallic alloys with transition metals are of high interest for their complex crystalline and quasicrystalline structures, formed primarily with late transition metals, and their technologically useful compounds. Experimental phase diagram determination is difficult because many phases often exist within small composition ranges, many structures have unusually large unit cells, and many are intrinsically disordered, exhibiting mixed or partial site occupancy.

First-principles calculations can help resolve some uncertainties in the phase diagrams but are challenging themselves, for many of the same reasons. Intrinsic disorder requires studying alternative realizations of specific site occupancy. Some of the nearby competing phases may have unknown or poorly known structures. The large unit cells pose computational difficulties. Further complicating the study is the prevalence of magnetism among late transition metals.

The Al-Fe system is the prototype binary magnetic alloy based on a bcc structure. The specific phase Al$_2$Fe$_2$ is important as it forms at the junction layers of Fe with Zn during galvanizing treatments. Our own interest in the Al-Fe phase diagram derives from its complex and disordered crystal structures, some of which are related to quasicrystals.

The compound Al$_2$Fe is of special interest because of its unusual lowest-possible symmetry crystal structure, triclinic with space group 1 (P1) as determined by Corby and Black. The initial crystallographic refinement, based on anomalous dispersion experiments, proposed an 18-atom unit cell (Pearson symbol aP18) with an unusual “hole” (see Fig. 1) that was sufficiently large to fit an entire Al or Fe atom. They also reported three sites of mixed occupancy, Al$_5$Fe$_{0.5}$.5

Our preliminary first-principles calculations of total energy$^7$ showed that filling the hole was energetically favorable; thus we predicted the correct Pearson type as aP19. However, we found this structure to be unstable with respect to competing phases, no matter how the hole was filled and how the partial occupancy was resolved. A hypothetical tetragonal structure based on the MoSi$_2$ prototype (Pearson symbol tI6) was predicted to be the true stable structure. This tI6 structure can be considered as an Al-rich variant of the B2 (Pearson cP2) structure of AlFe. It has never been observed experimentally, although it would be of high interest because it is predicted to be electrically insulating with a narrow gap.$^{45}$ Instead, multiple reexaminations confirm the stability of a triclinic structure for Al$_2$Fe. A recent crystallographic refinement,$^6$ utilizing conventional single-crystal diffraction, proposes that the space group is 2 (P1) and fills the hole, confirming our predicted Pearson type aP19.

Al$_5$Fe$_2$ has an orthorhombic structure (Pearson type oC24; see Fig. 2) featuring a rigid framework of fully occupied Al and Fe sites as well as partially occupied Al sites confined within channels$^7$ that thread through the structure. Our optimal assignment of atoms to the partially occupied sites is predicted to be weakly unstable to decomposition into competing phases, including the hypothetical tetragonal structure.

Here we present a thorough study of the stability of Al$_2$Fe and Al$_5$Fe$_2$ utilizing first-principles total energy calculations of low-temperature enthalpy supplemented by a phonon-based calculation of vibrational entropy yielding the high-temperature Gibbs free energy. Our calculations predict that the triclinic and orthorhombic structures are stabilized by vibrational entropy over the tetragonal structure at elevated temperatures. This occurs because aP19 has a much lower atomic density than tI6, and in oC24 the channel Al atoms are weakly bound and can actually diffuse at high temperature. A similar stabilization effect due to vibrational entropy was observed in the $\theta/\theta'$ system of Al$_2$Cu.$^8$

The remainder of this introduction surveys the global Al-Fe phase diagram and presents our calculational methods. We then present a thorough investigation of the energetics of plausible aP18 and aP19 structures, including the effects of magnetic moment formation and antiferromagnetism. Addressing Al$_5$Fe$_2$, we optimize the placement of Al atoms...
among partially occupied channel sites. Finally we present vibrational densities of states that display large enhancements of low-frequency phonons in the aP19 and oC24 structures relative to tI6, explaining high-temperature stability.

A. Assessed Al-Fe phase diagram

The Al-Fe phase diagram\(^9\) contains at least six compounds as well as the two pure elements. Additionally there are at least three known metastable phases. Table I displays pertinent information including names, composition ranges, Pearson types, space groups, and assessed stability of all reported phases. Explicit coordinates and energies of all structures considered are posted in the "published" area of our alloy website.\(^10\) Several of the phases report composition ranges associated with chemical substitution between Al and Fe and also partial site occupancy. The Al\(_3\)Fe phase, more accurately described as Al\(_{13}\)Fe\(_{4}\), is well known as a decagonal quasicrystal approximant. Structures of Al\(_2\)Fe and Al\(_5\)Fe\(_2\) also feature pentagonal networks.\(^11\)

B. Methods

Our calculations follow methods outlined in a prior paper.\(^12\) We utilize VASP\(^13\) to carry out first-principles total energy calculations in the PW91 generalized gradient approximation. Comparisons with the LDA and PBE density functionals confirm the principal findings based on PW91. We relax all atomic positions and lattice parameters, and increase our \(k\)-point densities until energies have converged. We adopt projector augmented wave potentials\(^15,16\) and maintain a fixed energy cutoff of 267.9 eV (the default for Fe). All calculations considered the possibility of spin polarization, and utilize a medium precision setting which allows small wrap-around errors in Fourier transforms.

Given total energies for a variety of structures, we calculate the enthalpy of formation \(\Delta H_{\text{for}}\) which is the enthalpy of formation \(\Delta H_{\text{for}} = H(\text{Al}\_m\text{Fe}_n) - [xH(\text{Fe}) + (1-x)H(\text{Al})], \quad (1)\)

where all enthalpies are per atom. Vertices of the convex hull of \(\Delta H(x_{\text{Fe}})\) constitute the predicted low-temperature stable structures. For structures that lie above the convex hull we confirm the principal findings based on PW91. We relax all calculations in the PW91 generalized gradient approximation.

II. RESULTS
A. Global phase diagram

As illustrated in Fig. 3 our calculated enthalpies agree in almost every respect with the assessed phase diagram. All the phases that are known to be stable at low temperature (heavy circles) indeed reach the convex hull. Those known to be metastable (diamonds) or stable only at high temperatures (light circles) lie slightly above the convex hull. Of those whose low-temperature stability is uncertain (triangles), Al3Fe lies on the convex hull, while Al5Fe2 and Al2Fe (aP18 and aP19) both lie slightly above.

The only serious discrepancy between the experimental phase diagram and our calculation is the presence of Al2Fe in the tI6 (prototype MoSi2) structure on the convex hull. This structure can be considered as a B2 (CsCl) structure with periodic stacking faults reversing the chemical order.

Its electronic density of states (see Fig. 4) exhibits a narrow gap.

Magnetism was found to be favorable in all the structures reported in Table I containing more than 33% Fe. Elemental Fe exhibits ferromagnetism in its low-temperature cI2 structure and modulated antiferromagnetism in its high-temperature cF4 structure. Al3Fe also exhibits long-wavelength antiferromagnetism in its aP18 and aP19 structures.

Our calculated total energies correctly predict the Al9Fe2 and Al2Fe structures to be metastable in the Al-Fe alloy system, while the same structures are correctly predicted to be stable in the Al-Co and Al-Mn alloy systems, respectively.3,17 Similarly, we correctly predict Al-Fe to be unstable when placed in the Al11Mn4.aP15 and Al5Co2.hP24 structures. Conversely, we correctly predict AlFe3 stable in Al-Fe but unstable in both Al-Co and Al-Mn. This sensitivity to the small differences in interatomic bonding between Fe and its neighbors in the
periodic table, Co and Mn, gives us confidence in the validity of our first-principles total energies.

B. Al$_2$FeCaP$_{18}$/aP$_{19}$

The Corby and Black$^2$ structure with Pearson type aP$_{18}$ possesses an unusually large hole. In addition three sites, labeled M1, M2, and M3, exhibit mixed Al$_{0.5}$Fe$_{0.5}$ occupancy (marked in green in Fig. 1). We tested all eight arrangements of Al and Fe among these three sites (labeled AAA, AAF, . . . , FFF) within a single unit cell and found that none of them resulted in a stable structure. Additionally, all suffered rather large maximum atomic displacements of 0.3–0.4 Å. All structures except AAA favored weak ferromagnetism. Our optimal stoichiometric structure, AFA, exhibited magnetic moments averaging 1 $\mu_B$/Fe atom, resulting in an energy drop of 26 meV/atom.

Previously,$^3$ we found that filling the Corby-Black hole with an Fe atom is energetically favorable, suggesting that aP$_{19}$ is the correct Pearson type for this compound. The nominal occupancy 0.24). The electronic density of states features a weak pseudogap while creating a magnetic moment on the channel Fe atom$^{21}$ of 2.2 $\mu_B$.

Our optimal structure would sit on the convex hull of enthalpy if it were not for the presence of the tI$_6$ structure. Instead, it sits 1.5 meV/atom above the tie line joining Al$_3$Fe (mC102) to Al$_2$Fe (tI$_6$), indicating that at low temperatures it will decompose into these structures.

III. VIBRATIONAL AND CONFIGURATIONAL FREE ENERGIES

Despite extensive effort, we were unable to find enthalpy-minimizing structures for Al$_3$Fe or for Al$_3$Fe$_2$. All structures considered remained above the convex hull, as illustrated in Fig. 3. Given that the assessed phase diagram does not assert low-temperature stability, we now consider the possibility that this structure is stabilized at high temperature by entropy. An entropy $s$ per atom results in a free-energy reduction of $Ts$ at temperature $T$. The obvious source of entropy is vibrational, arising from the low atomic density of aP$_{19}$ and the Al channels of oC$_{24}$.

The vibrational free energy can be obtained within the harmonic approximation by means of the quantum mechanical theory of phonons. For each phonon mode of vibrational frequency $\omega$, the temperature-dependent vibrational free energy (including zero-point energy, internal energy, and entropy) is

$$\ln \left[ 2 \sinh \left( \frac{\hbar \omega}{2k_B T} \right) \right].$$

We then integrate this quantity over frequency, weighted by the vibrational density of states $g(\omega)$ to obtain the full vibrational free energy

$$f_{vib}(T) = k_B T \int g(\omega) \ln \left[ 2 \sinh \left( \frac{\hbar \omega}{2k_B T} \right) \right] d\omega. \quad (2)$$
To calculate \( g(\omega) \) we employed the force constant method for phonon calculations, in which we take a supercell of minimum edge length 8 Å and evaluate the second derivatives of total energy \( \hat{\epsilon}^2 U/\partial \mathbf{R}_i \partial \mathbf{R}_j \) for all pairs of atoms \( i \) and \( j \). The calculations utilized density functional perturbation theory as implemented in VASP, and employ an accurate precision that avoids Fourier transform wrap-around errors. We then construct the dynamical matrix \( D(k) \) on a dense mesh of \( k \)-points and evaluate the phonon frequencies. The resulting calculated vibrational densities of states are presented in Fig. 4.

Even with the hole filled, the atomic volume of Al\(_2\)Fe in the aP19/FFFA structure is 13.48 Å\(^3\)/atom while the atomic volume of tI6 is only 12.7 Å\(^3\)/atom. The higher atomic volume of aP19 implies weaker bonding, consistent with lower enthalpy of formation. Weaker bonding suggests an enhanced density of low-frequency phonons that can increase vibrational entropy and correspondingly lower the vibrational free energy. Because Al\(_2\)Fe.aP19/FFFA is at very nearly the identical composition to Al\(_2\)Fe.tI6, we need only compare the vibrational free energies of these two structures (in principle we should include a small admixture of AlFe.cI2, but with very low weighting). The excess density of low-frequency phonons is clearly evident over the frequency range 10–30 meV and yields a reduction in free energy of 38 meV/atom by the time we reach \( T = 1000 \, \text{K} \). Comparing the free energies of tI6 and oP19, we find that oP19 is stabilized over tI6 for temperatures greater than 380 K.

For Al\(_2\)Fe\(_2\) in the optimal oP44 structure, we see an excess density of low-frequency phonons in the range 5–10 meV that leads to a free-energy reduction of 20 meV/atom by the time we reach \( T = 1000 \, \text{K} \). These phonon modes are localized in the channel Al atoms and are primarily polarized along the c axis. That is, they correspond to oscillations along the channels. These low-frequency modes are able to create an appreciable excess entropy at temperatures as low as 30 K. Comparing the free energies with the weighted average of mC102 and tI6, we find that oC24 is stabilized for temperatures greater than 320 K.

IV. CONCLUSION

This paper addresses the stability of two phases Al\(_2\)Fe (oP18/19) and Al\(_2\)Fe\(_2\) (oC24) that are experimentally observed in the Al-Fe phase diagram. These phases are predicted as unstable according to first-principles calculations, which instead predict stability of a hypothetical (and so far never observed) structure based on the prototype MoS\(_2\) (tI6). We show that each of the observed phases may be stabilized over the hypothetical one at high temperatures by their vibrational entropy. The high vibrational entropy arises from anomalously low atomic density in the case of oP19, and from diffusion of Al atoms within channels in the case of oC24. Presumably the high-temperature stability of the observed phases inhibits formation of the low-temperature tI6 phase because atomic diffusion is slow at the low temperatures at which it is stable. It would be very interesting if this predicted low-temperature phase can be formed, because it is expected to be a semiconducting compound formed from good metals.

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