Fe–X binary phase diagrams

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Iron forms binary alloys with a remarkably large number of elements. Some of the best-known examples combine Fe with another transition metal: Fe–Cr, Fe–Ni and Fe–Co, for instance, form the basis of many technologically important steels and magnetic materials.

In this project, we will investigate a different family of Fe-based binary alloys, in which the second element X is a **p-block element from groups 13 or 14 of the periodic table**. We will consider four systems:

$$X = \text{Al},\ \text{Si},\ \text{Ga},\ \text{or Ge}.$$

The best-known technological example is Fe–Si. Fe–Si alloys containing a few percent Si are used on a very large scale as **electrical steels**, for example in transformer cores, electric motors and generators. Fe–Al alloys and the ordered iron aluminide Fe_3Al are of interest because of their relatively low density and good oxidation and corrosion resistance. Fe–Ga alloys, commonly known as **Galfenol**, are magnetostrictive materials with applications in sensors, actuators and energy-harvesting devices. Fe–Ge alloys are technologically less established, but are actively studied for their magnetic, magnetostrictive and electronic properties.

These four systems share a feature that will be a cornerstone for this project. Around the composition Fe_3X, corresponding to 25 at.% X, an important ordered structure is the **D0$_3$** structure (Fig. 1). D0$_3$ is an ordered derivative of the bcc lattice: the atoms still occupy sites of an underlying bcc lattice, but Fe and X are no longer randomly distributed over those sites. At the ideal Fe_3X composition, one quarter of the sites are occupied by X in a regular pattern.

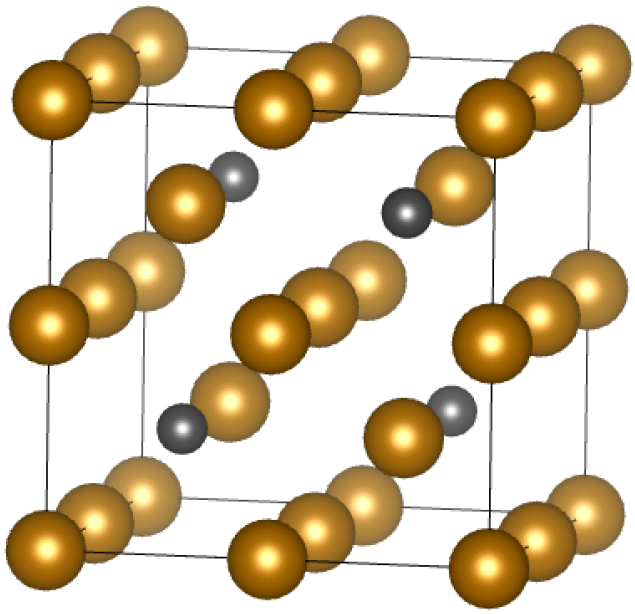

Figure 1: The D0$_3$ crystal structure of Fe_3X, shown as an ordered decoration of the underlying bcc lattice. This picture shows a 2x2x2 supercell of the conventional bcc cube, and the X-atoms form a tetrahedron on the 8 body-centered positions.

There is an important subtlety here. The D0$_3$ structure does **not** have exactly the same

thermodynamic status in all four phase diagrams. In Fe–Si it is a well-established equilibrium ordered phase over part of the phase diagram. In Fe–Al, the related $Fe_{13}Al_4$ phase is more stable, but we will consider $D0_3$ as a useful approximation. In Fe–Ga, on the other hand, $D0_3$ ordering can be metastable relative to competing structures such as $L1_2$, depending on composition, temperature and thermal history. Fe–Ge also contains competing ordered structures. Discovering and understanding such differences is part of the project.

1 The problem

We will zoom in on the **Fe-rich part of the binary phase diagram, from 0 to 25 at.%** X. At one end lies bcc Fe. At the other end we will use ordered $D0_3$-Fe_3X as the reference structure.

What happens between these two compositions?

Does X simply occupy Fe sites more or less randomly? Are particular ordered arrangements energetically preferred? Are there compositions at which a previously overlooked ordered crystal is especially stable? Can DFT predict ordered structures that are difficult to observe experimentally?

At first sight, the possibility of finding something new in such simple binary systems may seem surprising. After all, Fe, Al, Si, Ga and Ge are common elements and their binary phase diagrams have been studied for many decades.

There is, however, a complication. An experimental alloy is typically produced at high temperature and subsequently cooled. At sufficiently high temperature, atoms can diffuse through the crystal and explore many different arrangements. As the temperature decreases, diffusion becomes progressively slower. Eventually the atomic configuration becomes kinetically frozen on experimental timescales.

Suppose that a particular ordered arrangement has a slightly lower free energy than the disordered alloy. Thermodynamics then favours the ordered state, but reaching it requires sufficiently many atoms to diffuse to the correct lattice sites. If diffusion has already become extremely slow, the alloy may remain trapped in a **metastable** configuration for a very long time (weeks, years, centuries, ...). The structure that is observed experimentally therefore need not always be the lowest-energy structure accessible to the same atoms.

DFT gives us another way to attack this problem. We can construct a proposed atomic arrangement directly and calculate its energy without waiting for atoms to diffuse into that arrangement. We can therefore compare many possible orderings and search for particularly low-energy configurations.

There is an important limitation to keep in mind. The DFT calculations performed here are essentially **zero-temperature energy calculations**, whereas an experimental phase diagram describes equilibrium as a function of temperature. Configurational, vibrational and magnetic entropy can alter phase stability at finite temperature. A disagreement between a calculated zero-temperature convex hull and an experimental finite-temperature phase diagram is therefore not automatically an error: understanding the reason for such differences is itself part of the physics.

In this project, you will hunt for low-energy ordered structures in the range

$$0 \leq x_X \leq 25 \text{ at.}\%$$

of one of the Fe–Al, Fe–Si, Fe–Ge or Fe–Ga systems.

We will restrict the search to **substitutional bcc-derived alloys**: Fe and X occupy sites of the same underlying bcc lattice. Geometry optimization may slightly move the atoms and change the lattice parameters, but the starting configurations are generated by decorating bcc lattice sites with Fe and X, and the final configurations are usually not dramatically different from these.

Each team chooses one of the four binary systems. If there are more than four teams, the same system may be studied independently by several teams.

2 Step 1 — Converge your DFT calculations

Start with the provided Fe_7X structure, containing 12.5 at.% X. This composition lies approximately in the middle of the concentration interval that we will investigate.

Perform a convergence study with respect to:

- basis-set size;
- k-point sampling.

Increase the numerical accuracy until the calculated **pressure is converged to within a few kbar**. Use the resulting settings throughout the rest of the project. When changing the size or shape of a unit cell, adapt the k-point mesh so that the reciprocal-space sampling remains approximately equally dense.

The procedure for convergence testing is discussed in the *Let's play* module, DFT part 2.

Iron is magnetic, so perform these calculations **spin-polarized**. Take care that your calculations converge to a physically sensible magnetic solution.

3 Step 2 — Characterize the two end points

We will first establish reference data for the two ends of the investigated composition interval:

- bcc Fe;
- $D0_3$-Fe_3X.

For both structures, calculate an $E(V)$ curve and fit an appropriate equation of state.

Determine and report:

- the equilibrium volume, preferably also expressed per atom;
- the bulk modulus;
- the magnetic moment or magnetization, clearly stating which quantity and units you use.

How do these quantities change when 25% of the Fe atoms are replaced by X in the ordered $D0_3$ arrangement?

Do the equilibrium volume and bulk modulus increase or decrease? What happens to the magnetism? Try to connect your observations to the chemistry of the alloy rather than merely reporting numerical differences.

For systems in which $D0_3$-Fe_3X is metastable experimentally, it should nevertheless be calculated here: it provides a well-defined bcc-derived reference structure that can be compared across all four projects.

4 Step 3 — Find out what experiment already knows

While the first calculations are running, investigate the **experimental Fe–X binary phase diagram**.

Concentrate on the Fe-rich interval from 0 to 25 at.% X, but inspect the full phase diagram sufficiently well to understand what happens around it.

Discuss questions such as:

- Which phases have been experimentally identified in this concentration range?
- Which of them are ordered and which are disordered?
- Are A2, B2 or $D0_3$-type structures present?
- Are there order–disorder transformations?
- Are there miscibility gaps or two-phase regions?
- Are there important structural phase transitions?
- Where relevant, how do magnetic transitions such as the Curie or Néel temperature interact with the structural phase diagram?
- Are there known metastable phases?
- Does the reported phase diagram depend strongly on sample preparation or thermal history?

Also search for experimental values of the equilibrium lattice parameters or atomic volumes and bulk moduli of bcc Fe and Fe_3X, where such data are available, and compare them with your calculations.

Use reliable scientific literature and give proper references.

5 Step 4 — Start populating the phase diagram with DFT

We now start searching systematically for ordered bcc-based alloys.

Use **two series of supercells**:

1. $n \times n \times n$ supercells of the conventional two-atom bcc unit cell;
2. $n \times n \times n$ supercells of the one-atom primitive bcc unit cell.

For a conventional-cell supercell there are $2n^3$ atomic sites; for a primitive-cell supercell there are n^3 sites.

For each supercell, replace **one Fe atom by** X. Because the parent lattice consists entirely of symmetry-equivalent Fe sites, all single-substitution choices within a given undistorted supercell are equivalent.

Use $n = 1, 2, 3, \ldots$, but retain only structures whose composition lies inside the investigated interval of at most 25 at.% X. Continue to values of n that remain computationally reasonable.

Fully relax each structure using the converged settings from Step 1.

Calculate its **formation energy per atom**, using the elemental ground states as your reference states, and plot the formation energy as a function of X concentration.

Consider:

- Are the formation energies positive or negative?
- What does the sign of the formation energy tell you?
- How regularly do the concentrations generated by this procedure cover the interval from 0 to 25 at.%?
- Why does increasing the supercell size rapidly generate many points close to pure Fe but relatively few at intermediate compositions?

Your graph will be the central figure to which you will add results during the remainder of the project.

6 Step 5 — The number-crunching phase

We now make the configurational search much richer.

Return to the same supercells, but this time replace **two Fe atoms by X**.

Unlike the single-X case, there are now generally several inequivalent ways to choose the two sites. Two configurations that merely differ by a translation, rotation or another symmetry operation of the parent lattice are physically equivalent and should not both be calculated.

Find a systematic way to generate the **symmetry-inequivalent configurations** without unnecessary duplicates. You may do this by careful geometrical reasoning, by writing a small program, or by using an appropriate symmetry-analysis tool. Whatever method you use, explain it clearly.

Calculate and relax as many of these structures as reasonably possible.

If time, computer resources and courage permit, continue with three X atoms, four X atoms, and so on. Always restrict your final analysis to the 0–25 at.% interval.

Add every calculated formation energy to your graph.

6.1 Construct the convex hull

Use your calculated energies to construct the **lower convex hull**.

A structure on this hull is stable against decomposition into the other structures represented in your dataset. A structure above the hull is unstable with respect to an appropriate combination of lower-energy structures; its vertical distance from the hull is the **energy above hull**.

Be careful with the interpretation. Your search is restricted to a finite set of bcc-derived configurations. A structure that lies on your calculated hull is therefore a **candidate ground-state structure within the space you explored**. Demonstrating true thermodynamic stability would require comparison with every competing structure, including non-bcc structures that may occur in the real Fe–X phase diagram.

As you calculate more configurations, watch how the hull evolves. Does it quickly stop changing, or do newly calculated structures continue to replace previous hull vertices?

If you identify a particularly low-energy ordered structure at a composition that is not represented by a known experimental phase, you may have found an interesting predicted ground-state candidate.

6.2 Volume and Vegard's law

For every relaxed configuration, also record its equilibrium volume per atom.

Plot equilibrium volume as a function of X concentration.

Look up **Vegard's law**. What would you expect the concentration dependence of the volume to look like if Vegard's law were obeyed? Does your calculated system follow this behaviour? Are the deviations systematic? Do different atomic orderings at the same composition produce noticeably different equilibrium volumes?

6.3 Characterize new hull structures

If you find additional ordered structures on your convex hull, calculate an $E(V)$ curve for each of them and determine their bulk modulus.

Compare these values with those of bcc Fe and $D0_3$-Fe_3X.

Finally, compare your calculated zero-temperature results with the experimental phase diagram studied in Step 3.

Which features agree? Which do not?

For disagreements, consider several possible explanations:

- incomplete sampling of atomic configurations;
- competing crystal structures outside the bcc family;
- finite-temperature configurational entropy;
- lattice vibrations;
- temperature-dependent magnetism;
- limitations of the DFT approximation;
- experimental kinetic trapping and metastability.

Do not merely state that calculation and experiment disagree: try to explain **why**.

7 Step 6 — The optional and challenging phase: can you search smarter?

By now you will have discovered the main weakness of brute-force searching: the number of possible atomic decorations grows extremely rapidly with supercell size.

To be reasonably confident that you have explored all relevant orderings, you could easily require **thousands or millions of configurations**. Performing a fully converged DFT geometry optimization for every one of them is impractical.

Can we do better?

Investigate computational strategies that can search configurational space much more efficiently.

A particularly natural approach for this project is a **cluster expansion**. Because all configurations can be viewed as different Fe/X occupations of the same underlying bcc lattice, a relatively small training set of DFT calculations can in principle be used to construct an effective model that predicts the energies of a much larger number of configurations at negligible computational cost.

Other possibilities include surrogate or machine-learning models, active-learning strategies, genetic or evolutionary searches, and other schemes that decide intelligently which configurations deserve an expensive DFT calculation.

Investigate at least one such strategy and, if possible, implement it for your Fe–X system.

Can your accelerated search find a lower-energy structure that you missed during the brute-force stage?

And can the method do more than identify zero-temperature structures—for example, could it eventually be extended to investigate **finite-temperature ordering and order–disorder transitions**?

8 Reporting your results

The purpose of the project is not simply to produce a large collection of DFT calculations. Your goal is to use those calculations to build a coherent physical picture of the Fe-rich part of your binary system:

> **Which atomic arrangements are energetically preferred, why are they preferred, and how do the predictions of zero-temperature DFT relate to the experimentally observed phase diagram?**

Your calculations, analysis and interpretation should be presented in a **scientific paper** and a **video**, following the instructions in the *Project* tile at www.compmatphys.org.

Information about the intermediate and final deadlines can be found in the *Quick Start* tile.

9 Source files

At the course page where you found the present file, a source file with a few starting cif files is available.