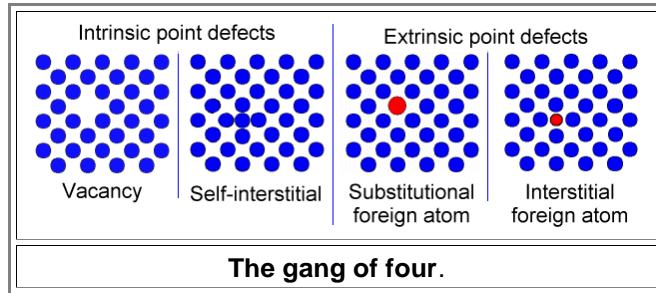


## 5.2.1 Point Defects

### 5.2.1 The Gang of Four

We start with **zero-dimensional defects**; the smallest denizens of the defect zoo. Here they are - *all four of them*:



It's pretty simple. More than those four "**point defects**" we cannot make by playing with atoms inside an **elemental crystal**, meaning a crystal made from just one of the elements like iron or silicon.

The question we need to answer now is "*why*" and "*how many*"?

*Why* should a crystal contain those defects and if there is some reason, *how many* should it be?

Well, we already know that any crystal can and will **make vacancies** because it needs to produce disorder to achieve nirvana. If you [glimpse ahead](#) a little bit, you can see *how* the crystal makes vacancies.

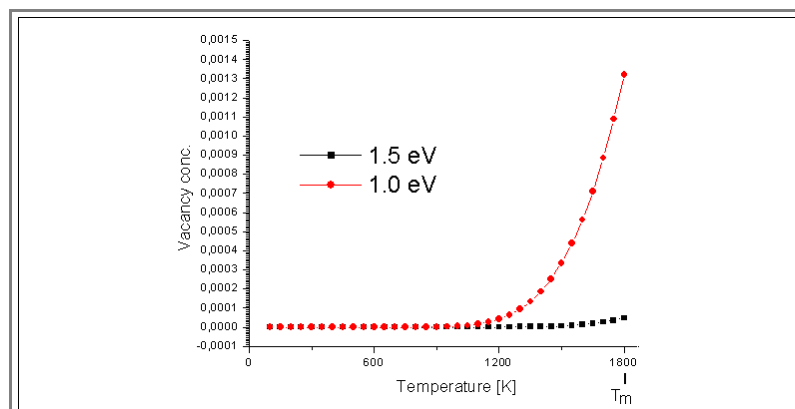
For exactly the same reasons —creating increasing disorder with increasing temperature— it also can and will make "**self-interstitials**", atoms of its *own kind* that squeeze themselves into the interstices or interstitial positions in the lattice.

The first question thus finds an easy answer for two of the four point defects. We are left with figuring out how *many* vacancies and self-interstitials we must have at some temperature.

Disorder is more important at high temperatures. This can only mean that the [number or the concentration](#) of both vacancies and self-interstitials must increase with increasing temperature. If you bothered to look at the [science module about vacancies](#), you know that the concentration increases *exponentially*. If you didn't, you may want to check the "science" module to get some idea what "**exponential growth**" means.

Just a hint: If you hate exponentials and logarithms but like money, you should reconsider. It's those dreaded math objects that will tell you how your money will go down the drain with the coming inflation (or through the roof if you invest it wisely).

OK—for those of you who can't overcome their fear of math: Exponential growth of the vacancy concentration with temperature means that the concentration goes up *rapidly* with temperature. Here is a calculated curve showing the approximate vacancy concentration in iron as a function of temperature:



**Approximate vacancy concentration in iron as function of (absolute) temperature.  $T_m$ =melting point.**

In order to calculate curves like this one needs to know a parameter called "[vacancy formation energy](#)" that is not all that well known for iron. That's why there are two curves for the two values shown. The "real" curve is probably somewhere in between. 0.01 would be 1 %; 0.0001 is 1/100 of 1% or 100 ppm

[Science  
Module](#)

**Exponentials;  
logarithms**

● So, yes, the concentration is indistinguishable from zero over most of the temperature regime. Only at rather high temperatures it goes up rapidly. That doesn't mean that there is nothing at lower temperature, you just can't see it in this plot. If you plot the total earnings in your country versus time, your salary of 2.654 € (or of whatever your currency might be) this July will simply not show either—even so it was *very* meaningful to you. In the [science module](#) you can look up how to make better plots of vacancy concentration.

▶ OK—now you know more about vacancies than you ever fancied in your wildest dreams. How about *self-interstitials*?

● It is exactly the same thing. Self-interstitials do the same thing as vacancies: they introduce disorder and thus raise the entropy. They just don't do it quite as well as vacancies in almost all common crystals. Most crystals, including *all* metals, therefore prefer vacancies to self-interstitials by far, and only make a tiny amount of self-interstitials that we can *simply forget* about. Iron self-interstitials thus are completely unimportant to sword making and we won't mention them ever again (except in the [science module](#)).

● The big exception, by the way, is **Silicon** (Si). In silicon crystals the self-interstitial is of major importance. How that was found out and drummed into the heads of the non-believers, would be a long story of its own. I'd love to tell it because I had a hand in it. I will restrain myself here—but not in this [link](#).

▶ The vacancy and the self-interstitial are the two zero-dimensional defects that we subsume under "**intrinsic point defects**" for obvious reasons. "*Intrinsic*" is one of those fancy Latin words we scientists like to use in order to show off. It means "innate", or "incarnate" in the sense that the crystal needs nothing from the outside for making them—in contrast to the **extrinsic** (extraneous, foreign) point defects shown on the right in the figure above.

So let's look at the two *extrinsic* guys now, some foreign atom in an **interstitial** position, or some foreign atom at an **substitutional** position.

We also call them *impurity* or *dirt* atoms, and sometimes *doping* atoms or *alloying* elements, I'll come back to that.

● I know. Those names suck. If you can come up with better ones, let me know. And while you are at it, find better names for other outlandish expressions like: democracy, republicans, maitre'de, caucus, anonymous, dermatologists or ophthalmologist, too. Or simply accept that it's not worth the bother to rename things that already have good working names, however weird. All our intrinsic / extrinsic / interstitial / substitutional stuff is reasonably clear and you got to have some names, after all.

If you could live with things having names like "George Walker Bush", you shouldn't have a problem with dirt going by the name "substitutional foreign atom" either.

As far as dirt is concerned, foremost on our mind is of course ~~Berusee~~ carbon in iron. Carbon, it turns out, lives as an **extrinsic interstitial** in between the iron atoms as long as it is "**dissolved**", meaning incorporated as a *single atom*.

In *silicon*, carbon would be a *substitutional* foreign atom, replacing ("substituting") one of the silicon atoms, so it depends on the host crystal which of the two possibilities a given foreign atom will assume.

Let's summarize:

<b>Intrinsic point defects</b>	<b>Vacancy</b> <b>Self-interstitial</b>
<hr/>	
<b>Extrinsic point defects</b> (impurity atoms, doping atoms, dirt, alloy element...)	<b>Substitutional atom</b>  <b>Interstitial atom</b>

▶ When we talk about carbon in iron, we usually consider concentrations between 0 % and 1,5 %. Those are *always weight percent* (written wt % if you want to be precise) if not otherwise stated ([remember?](#)).

● This makes a lot of sense in material *engineering* because you can easily make desired mixes by *weighing* the ingredients.

In materials *science*, however, we look at *atoms*. In order to assess foreign atoms in a host crystal, we need their [concentration](#) in **atom percent** (at %). In other words, we want to know how many percent of all the atoms present are carbon atoms?

There is no easy way to switch from one to the other; consult the link for how it's done.

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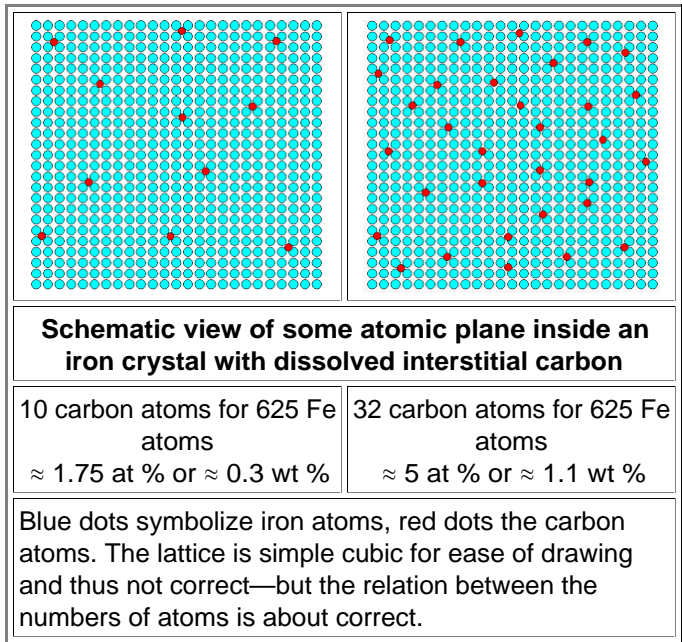
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[Basic link](#)

**Concentr.**  
**wt% ⇌ at%**

- If we take, for example, the "*magical*" 6.7 wt % of carbon and express it in atom percent, we get **6.7 wt % = 25 at %**. A quarter of all atoms then are carbon atoms. Why 6.7 wt % of carbon of carbon is "*magical*" we will [see later](#)—but you are welcome to make a guess, now that you know it corresponds to a mix of iron : carbon = 3 : 1 in terms of atoms. Hint: one could write that Fe<sub>3</sub>C.

What a *schematic* iron crystal would look like with 1.75 at % (≈ 0.3 wt %) or 5 at % (≈ 1 wt %), respectively, of carbon atoms *dissolved* in the volume of the iron, is schematically shown below.



You are looking at a virtual cut through the crystal, of course, and at any plane inside the crystal it would look like this, just with the carbon atoms distributed at random at interstitial positions. We also call this "*the carbon is dissolved*" or it is in **solid solution**.

Now why should that be virtual? I [stated some time ago](#) that there are special [microscopes](#) that allow you to look at the surface with atomic resolution. Yes—but:

If we look at a *real* surface of almost anything you wouldn't see much because a real surface of almost all crystals in air is *oxidized*. With an iron sample you always would look at "rust", even if to your eye it looks bright and shiny. An iron oxide layer just a few atoms thick, totally invisible to the eye, is all it takes to completely obscure a surface from atomic "view".

- Even if we use the common (and expensive) technique of putting our sample in ultra-high vacuum (*UHV*) where it can't oxidize, and "somehow" take off the original rust layer in there, we would still have a hard time seeing anything! Why? Because *iron is magnetic*! That tends to mess up many microscopes, including the STM we would need to employ here. I have therefore no iron surface pictures taken at atomic resolution that looks remotely like the schematic picture above. The best I can give you are [pictures](#) of point defects in a gallium arsenide (GaAs) surface.

Note that despite the rather small *weight percent* concentrations of about 0.3 wt% or 1 wt%, respectively, in the figures above, it's actually *quite a bit of carbon* if you think about it. Nevertheless, most "bonding springs" still connect iron atoms and thus [Young's modulus](#) is hardly changed relative to that of pure iron.

Note that this *not* a theoretical prediction open to some doubt. This is as hard a *fact* as you like them to come.

Now that we have played around a bit with an *extrinsic* defect like carbon in iron, the same question [as above](#) for the intrinsic defects comes up:

*Why* should a crystal contain those *extrinsic* defects, and if there is some reason, *how many* should it be?

- In an *ideal crystal world* the answers to those questions would be *exactly* the same as for intrinsic point defects:

- *Extrinsic* defects increase disorder, and a certain number of all the other 90 or so elements should be part of any nirvana-seeking crystal.
- The proper "nirvana" number of *extrinsic* defects depends, among other things, strongly on the temperature. Generally, the concentration should increase with increasing temperature.

- In an *ideal world* *you* would have the proper amount of money necessary for achieving your personal nirvana conditions. But neither you nor the crystal exist in an ideal world. A crystal cannot *make* foreign atoms at will, just as (most of) us cannot print money all that easily.

- So in the **real crystal world**, the answer to these questions is different from the one describing the **ideal** word. It is extremely simple but will have formidable consequences:

**You got it, you keep it!**

- Tough luck. The number of **any** atoms forming extrinsic point defects—interstitial carbon in iron, substitutional carbon in silicon, substitutional phosphorous in iron, ..., (the list here would contain about  $(90 \cdot 90)=8.100$  entries; can you see why?)—is whatever it is. Mostly that number simply comes from the original process used for **making** the material.

The **crystal** can neither make more foreign atoms or **impurities** if it wants too, nor can it **easily** get rid of the ones it has. It needs a little bit of help from friends like you for this task

The consequences are dramatic:

**If a crystal contains impurities in any form, it can no longer achieve absolute nirvana. Never. Ever.**

Our steel blade or crystal with 0,5 wt% carbon in it, or just any crystal containing impurities, is stuck now. It wants to have a certain precise number for nirvana but chances are extremely high that the number it actually has is far off that nirvana number.

The crystal is stuck. What is it going to do?

- Exactly what you would do if your 9 children are running all about the place, producing far more disorder than needed, and keeping you from achieving you preferred state of being (easy chair, peace and quiet, good wine, a good book like this one). You round 'em up and lock them into a room somewhere else. Crystals do the same thing; they imprison their impurity atoms or, as it is properly called, **precipitate** them. We will see how that works shortly. But before we do that I want to generalize a bit.

It should be clear that as far as extrinsic point defects go, we are not restricted to carbon. I can take whatever else the periodic table has to offer (about 90 elements) and put it into my iron. I know how to do it in reality, for you it's an easy thing to do in your brain lab.

Now let's look at how these impurities have settled in the iron. The good news is that the foreign atoms can assume only **three** different configurations:

1. They could be **dissolved** as **interstitial** impurity atom. Then they are somehow wedged in between the regular atoms.
2. They could be **dissolved** as a **substitutional** impurity atoms. Then they "substitute", i.e. replace an iron atom in the crystal lattice.
3. Only a few are dissolved in one of the two possible ways and and the rest is securely put away in a **precipitate** (I'll come to that shortly).

- Let's look at few examples

- Carbon (C), nitrogen (N), and hydrogen (H) are always dissolved as **interstitial impurity atoms in iron**.
- Phosphorus (P), Sulfur (S), Manganese (Mn), Nickel (Ni), Chromium (Cr), Vanadium (V) and most other atoms are always dissolved as **substitutional impurity atoms in iron**.
- Oxygen (O) and boron (B) can be dissolved in both ways.
- All of them will be imprisoned in precipitates if they exceed a certain specific concentration.

- **Which** elements we have inside the iron crystal, how **many**, and in what kind of **configuration** determines most of the important **properties** of your steel.

So, without a little bit of help, the concentration of **extrinsic** point defects—impurities— in crystals won't change, in contrast to the **intrinsic** point defects that the crystals can make and dispose of on its own.

This is great because that's where you and I come in. If you know how to do it, you can change the impurity concentration of a given crystal, no matter if the crystal likes it or not. That's where technology starts. Let's look at two examples:



- Building a silicon microprocessor or most anything else from *silicon* (Si) needs to start with a very clean and perfect silicon crystal, as close to nirvana as it can be. This involves producing extremely clean liquid silicon first. In a second step an almost perfect crystal is grown by rather involved methods. Then we *mess up the crystal* by putting substitutional impurities like phosphorous (P), arsenic (As), or boron (B) inside well defined parts of it. So the concentration of extrinsic point defects does change: it goes up. The crystal doesn't like it, of course, because that takes it rudely off his near-nirvana state of being. It fights back in many ways, and it fights dirty! That is one of the reasons why microelectronics technology is not a simple enterprise.
- When we make steel in modern times, we start with rather dirty liquid iron, it is actually *cast-iron*. We remove most of the unwanted dirt already in the liquid state and we add some wanted dirt. Crystallization is not controlled on a microscale so we get (huge) polycrystals. Certain processes in the solid crystalline state (like "case hardening") will change the concentration of some impurities (mostly carbon) to some extent.
- ▶ One last word to impurities in crystals. Without going into more details, one thing becomes clear: it is far easier to mess up a crystal than to keep it clean or to clean it up if its messy. It's not so difficult to get impurities inside. Crystals, after all, like to have some at high temperatures. It is just far more difficult or well-nigh impossible to get them out again.
- It is just the reverse of opening a can of worms, or squeezing tooth paste or your heir out of a tube. The problem there is to get the stuff back in.