

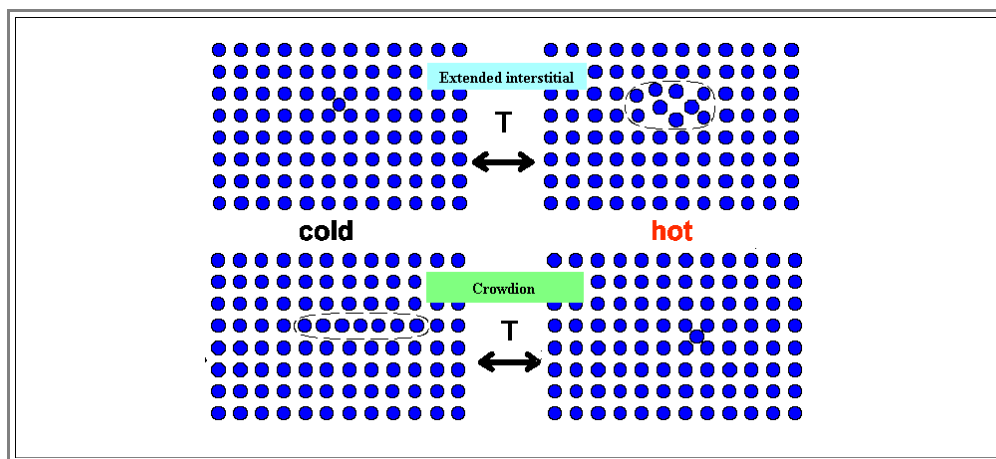
### 1.3.3 The larger View and Complications

#### Looking More Closely at Point Defects

- ▶ This subchapter means to show that even the seemingly most simple defects - vacancies and interstitials - can get pretty complex in real [crystals](#). This is already true for the most simple real crystal, the **fcc** lattice with one atom as a base, and very true for fcc lattices with two identical atoms as a base, i.e. **Si** or diamond. In *really* complicated crystals we have at least as many types of vacancies and interstitials as there are different atoms - it's easy to lose perspective.
  - To give just two examples of real life with point defects: In the seventies and eighties a bitter war was fought concerning the precise nature of the self-interstitial in elemental **fcc** crystals. The main opponents were two large German research institutes - the dispute was never really settled.
  - Since about **1975** we have a world-wide dispute still going on concerning the nature of the intrinsic point defects in **Si** (and pretty much all other important semiconductors). We learn from this that even point defects are not easy to understand.
- ▶ You may consider this sub-chapter as an overture to the point defect part of course: Some themes touched upon here will be taken up in full splendor there. Now let's look at some phenomena related to point defects
- ▶ We start with a simple [vacancy](#) or [interstitial](#) in (**fcc**) crystals which exists in [thermal equilibrium](#) and ask a few questions (which are mostly easily extended to other types of crystals):

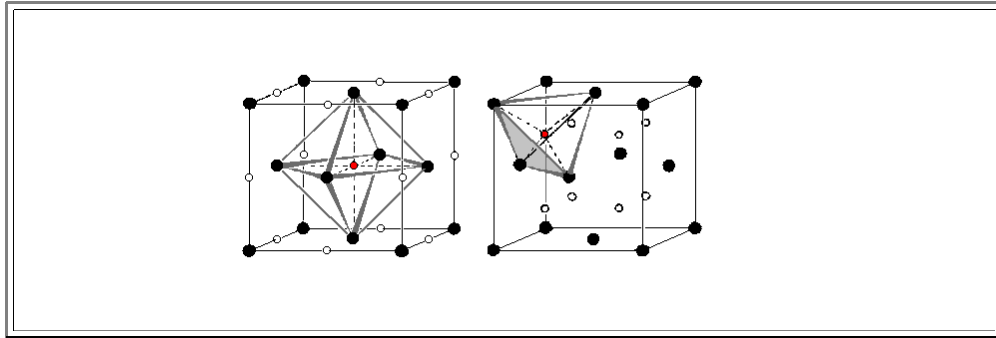
#### The atomic structure

- ▶ What is the *atomic structure* of point defects? This seems to be an easy question for vacancies - just remove an atom!
  - But how "big", how [extended](#) is the vacancy? After all, the neighboring atoms may be involved too. Nothing requires you to have only simple thoughts - let's think in a complicated way and make a vacancy by removing **11** atoms and filling the void with **10** atoms - somehow. You have a vacancy. What is the structure now?
  - How about interstitials? Let's not be unsophisticated either. Here we could fill our **11**-atom-hole with **12** atoms. We now have some kind of "**extended**" interstitial? *Does this happen?* (Who knows, it's possibly true in **Si**). How can we discriminate between "localized" and "extended" point defects?
  - With interstitials you have several possibilities to put them in a lattice. You may choose the [dumbbell](#) configuration, i.e. you put two atoms in the space of one with some symmetry conserved, or you may put it in the [octahedra](#) or [tetrahedra](#) interstitial position. Perhaps surprisingly, there is still one more possibility:
  - The "[crowdion](#)", which is supposed to exist as a metastable form of interstitials at low temperatures and which was the subject of the "war" mentioned above.
  - Then we have the **extended interstitial** made following the general recipe given above, and which is believed by some (including me) to exist at high temperatures in **Si**. Let's see what this looks like:



- ▶ Next, we may have to consider *the charge state* of the point defects (important in semiconductors and ionic crystals).
  - Point defects in ionic crystals, in general, must be charged for reasons of charge neutrality. You cannot, e.g. form **Na**-vacancies by removing **Na<sup>+</sup>** ions without either giving the resulting vacancy a positive charge or depositing some positive charges somewhere else.
  - In semiconductors the charge state is coupled to the energy levels introduced by a point defect, its position in the [bandgap](#) and the prevalent Fermi energy. If the Fermi energy changes, so does, perhaps, the charge state.
- ▶ Now we might have a *coupling between charge state and structure*. And this may lead to an athermal diffusion mechanism; something really strange (after **Bourgoin**).

- Just an arbitrary example to illustrate this: The *neutral* interstitial sits in the octahedra site, the *positively charged* one in the tetrahedra site (see below). Whenever the charge states changes (e.g. because its energy level is close to the Fermi energy or because you irradiate the specimen with electrons), it will jump to one of the nearest equivalent positions - in other word it diffuses *independently of the temperature*.



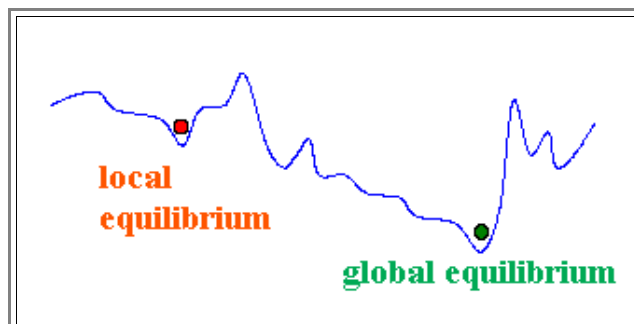
- These examples should convince you that even the most simplest of defects - point defects - are not so simple after all. And, so far, we have (implicitly) only considered the simple case of *thermal equilibrium*! This leads us to the next paragraph:

### But is there thermal equilibrium?

- The list above gives an idea what *could* happen. But what, actually, *does* happen in an ideal crystal in *thermal equilibrium*?
  - While we believe that for common fcc metal this question can be answered, it is still open for many important materials, including Silicon. You may even ask: *Is there thermal equilibrium at all?*
  - Consider: Right after a new portion of a growing crystal crystallized from the melt, the concentration of point defects may have been controlled by the growth kinetics and not by equilibrium. If the system now tries to reach equilibrium, it needs sources and sinks for point defects to generate or dump what is required. Extremely perfect **Si** crystals, however, do not have the common sources and sinks, i.e. dislocations and grain boundaries. So what happens? Not totally clear yet. There are more open questions concerning Si; activate the [link](#) for a sample.
- Well, while there may be some doubt as to the existence of thermal equilibrium now and then, there is no doubt that there are many occasions where we definitely do not have thermal equilibrium. What does that mean with respect to point defects?

### Non-equilibrium

- Global* equilibrium, defined by the *absolute* minimum of the free enthalpy of the system is often unattainable; the second best solution, *local* equilibrium where some local minimum of the free enthalpy must suffice. You always get non-equilibrium, or just a local equilibrium, if, starting from some equilibrium, you change the temperature.
- Reaching a new local equilibrium of any kind needs kinetic processes where point defects must move, are generated, or annihilated. A typical picture illustrating this shows a potential curve with various minima and maxima. A state caught in a local minima can only change to a better minima by overcoming an energy barrier. If the temperature  $T$  does not supply sufficient thermal energy  $kT$ , global equilibrium (the deepest minimum) will be reached slowly or - for all practical purposes - never.



- One reaction helpful for reaching a minima in cases where both vacancies and interstitials exist in non-equilibrium concentrations (e.g. after lowering the temperature or during irradiation experiments) could be the mutual annihilation of vacancies and interstitials by recombination. The potential barrier that must be overcome seems to be only the migration enthalpy (at least one species must be mobile so that the defects can meet).

- There might be unexpected new effects, however, with extended defects. If an localized interstitial meets an extended vacancy, how is it supposed to recombine? There is no local empty space, just a thinned out part of the lattice. Recombination is not easy then. The barrier to recombination, however, in a kinetic description, is now an **entropy barrier** and not the common energy barrier.

Things get really messy if the generation of point defects, too, is a non-equilibrium process - if you produce them by crude force. There are many ways to do this:

- **Crystal Growth** As mentioned above, the incorporation of point defects in a growing interface does not have to produce the equilibrium concentration of point defects. An "easy to read" paper to this subject (in German) is available in the [Link](#)
- **Quenching**, i.e. **rapid cooling**. The point defects become immobile very quickly - a lot of sinks are needed if they are to disappear under these conditions - a rather unrealistic situation.
- **Plastic deformation**, especially by dislocation climb, is a non-equilibrium source (or sink) for point defects. It was (and to some extent still is) the main reason for the degradation of Laser diodes.
- **Irradiation** with electrons (mainly for scientific reasons), ions (as in ion implantation; a key process for microelectronics), neutrons (in any reactor, but also used for **neutron transmutation doping of Si**),  $\alpha$ -particles (in reactors, but also in satellites) produces copious quantities of point defects under "perfect" non-equilibrium conditions.
- **Oxidation of Si** injects **Si** interstitials into the crystal.
- **Nitridation of Si** injects vacancies into the crystal.
- **Reactive Interfaces** (as in the two examples above), quite generally, may inject point defects into the participating crystals.
- **Precipitation** phenomena (always requiring a moving interface) thus may produce point defects as is indeed the case: (**SiO<sub>2</sub>-precipitation** generates, **SiC-precipitation** uses up Si-interstitials).
- **Diffusion** of impurity atoms may produce or consume point defects beyond needing them as diffusion vehicles.

And all of this may critically influence your product. The **Si** crystal growth industry, grossing some **8 billion \$** a year, continuously runs into severe problems caused by point defects that are not in equilibrium.

- So-called [swirl-defects](#), sub-distinguished into **A-defects** and **B-defects** caused quite some excitement around **1980** and led the way to the acceptance of the existence of interstitials in **Si**.
- Presently, [D-defects](#) are the hot topics, and it is pretty safe to predict that we will hear of **E-defects** yet.

Now, most of the examples of possible complications mentioned here are from pretty recent research and will not be covered in detail in what follows.

- And implicitly, we only discussed defects in monoatomic crystals - metals, simple semiconductors. In more complicated crystals with two or more different atoms in the base, things can get really messy - look at [chapters 2.4](#) to get an idea.
- Anyway, you should have the feeling now that acquiring some knowledge about defects is not wasted time. Materials Scientists and Engineers will have to understand, use, and battle defects for many more years to come. Not only will they not go away - they are needed for many products and one of the major "buttons" to fiddle with when designing new materials