

STRUCTURE: Defects

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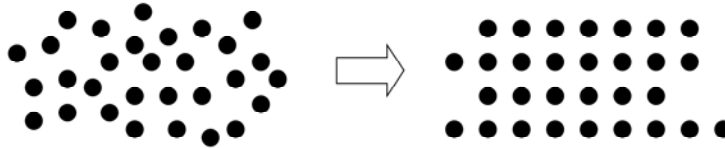
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Perfect crystalline solids are very rare. Solids include defects that affect their properties. Two chemically identical solids with different types and/or concentrations of defects will have different properties.

INTRODUCTION

Types of imperfections (or defects)



Classification of Defects:

- | | | |
|-----------|-------|------------------------|
| a. Point | (0-D) | Atomic size |
| b. Line | (1-D) | Lines of atoms |
| c. Area | (2-D) | Surfaces made of atoms |
| d. Volume | (3-D) | Volumes of atoms |

Special considerations:

- All properties are defect-limited
- Defect concentrations related to time and temperature
- Defects are higher energy than surrounding crystal



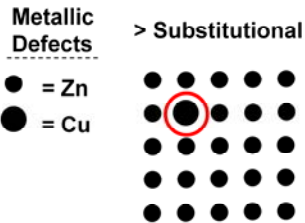
All materials, whether simple in structure (metals) or more complex (ceramics and polymers), will attempt to lower their total energy. Organization of the atomic or molecular components, while increasing the entropy, produces a significant reduction in enthalpy. So most things try to become organized – which generally means becoming crystallized. If the components of the structure are simple, crystallization occurs relatively quickly.

The objectives of this module are to examine the degree of perfection associated with crystallization. **[CLICK]** There are 4 levels we will consider – atoms, lines of atoms, planes of atoms, and volumes of atoms. Another way to imagine this is in terms of point defects (zero dimensional, 0D), line defects (one dimensional, 1D), area defects (two dimensional, 2D), and volume defects (three dimensional, 3D). At each level, the types and number of defects involved significantly affect the properties of materials. Thus, we talk about properties as being “defect-limited.” For the present time, we will focus primarily on the effects on mechanical properties.

[CLICK] The concentration (i.e., number) of defects depends on the conditions of crystallization – and are strongly related to the amount of TIME that was available and the TEMPERATURE (or thermal energy) of the system. Each defect is a zone that is at higher energy than the surrounding more well-organized material.

POINT DEFECTS

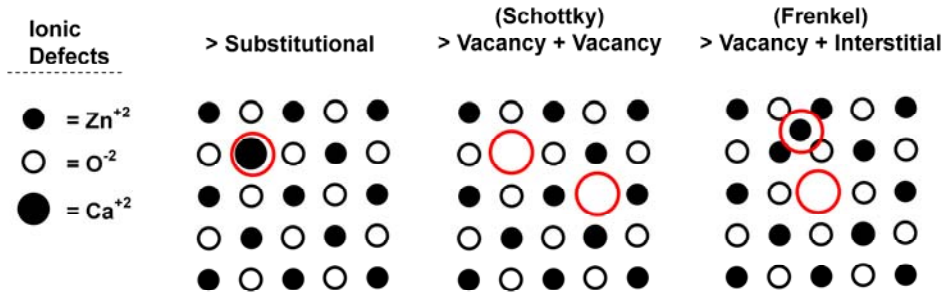
Metallic Vacancy, Substitutional, Interstitial, Self-Interstitial Defects



Imagine a crystal made up of Zn atoms in a cubic arrangement. **[CLICK]** Now remove one of the zinc atoms and substitute it with a larger Cu atom. It will not be the same size and will locally disturb the arrangement. This is a SUBSTITUTIONAL defect. Most pure metals are not 100% of one type of atom. Their impurities can produce substitutional defects. **[CLICK]** Now imagine that one of the Zn atoms is removed and not replaced. **[CLICK]** The resulting defect is a VACANCY. **[CLICK]** Next imagine that one of the Zn atoms is misplaced and exists between others in the regular arrangement. **[CLICK]** This atom is in an SELF INTERSTITIAL position. **[CLICK]** If the atom in the interstitial site is a different type, **[CLICK]** it is just called an INTERSTITIAL.

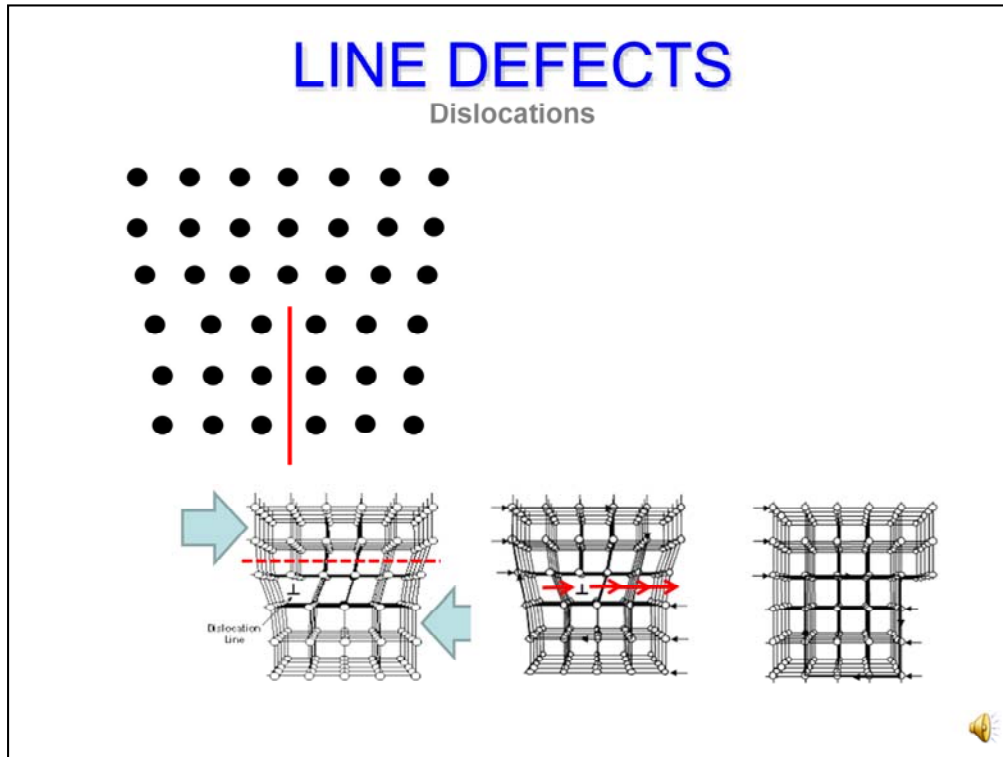
POINT DEFECTS

Ionic vacancy, Substitutional, Interstitial, and Self-Interstitial Defects



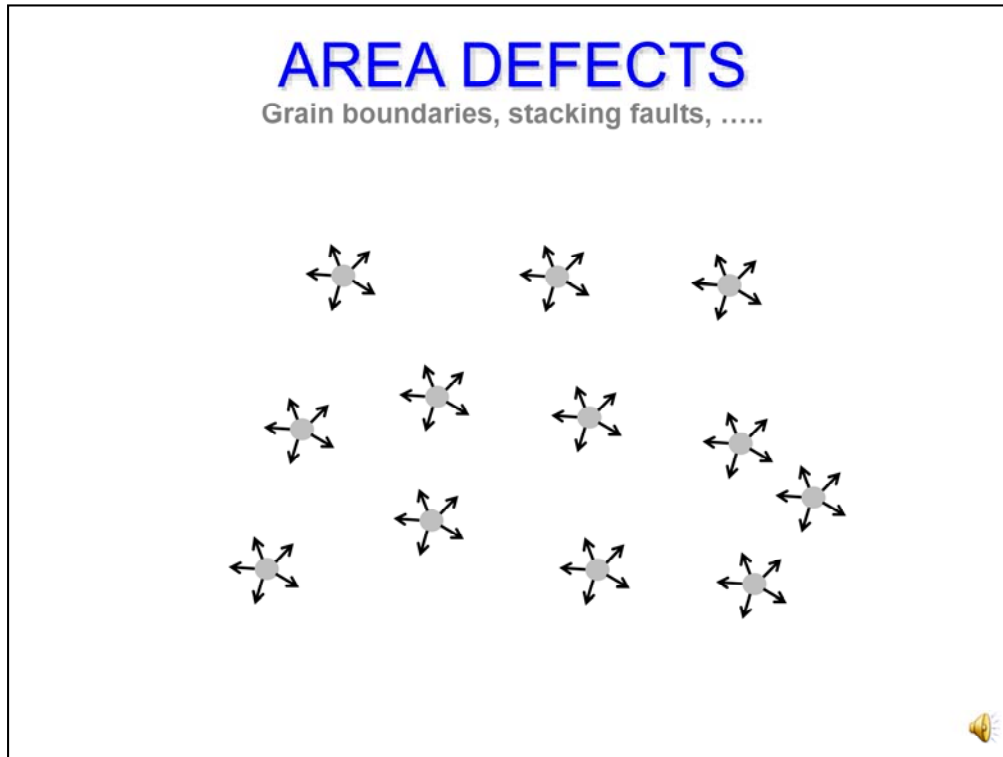
Exactly the same types of defects are present in ionic crystals as well, except that in order to maintain a charge balance, a defect must often be accompanied by a counterbalancing one. Look at the example show for an ionic lattice for ZnO which contains Zn^{+2} ions and O^{-2} ions. You can always substitute a +2 or -2 ion with another one. **[CLICK]** In the figure a Ca^{+2} ion is a substitutional defect that replaces a Zn^{+2} ion. However, if you take one ion type out, you must take one of the other type out as well, or make some other adjustment to maintain charge balance.

[CLICK] A vacancy paired with a vacancy is called a Schottky defect. **[CLICK]** An self-interstitial paired with a vacancy is called a Frenkel defect. You are not responsible for knowing these particular terms, but you should understand that point defects become more complex as charge balance considerations come into play.



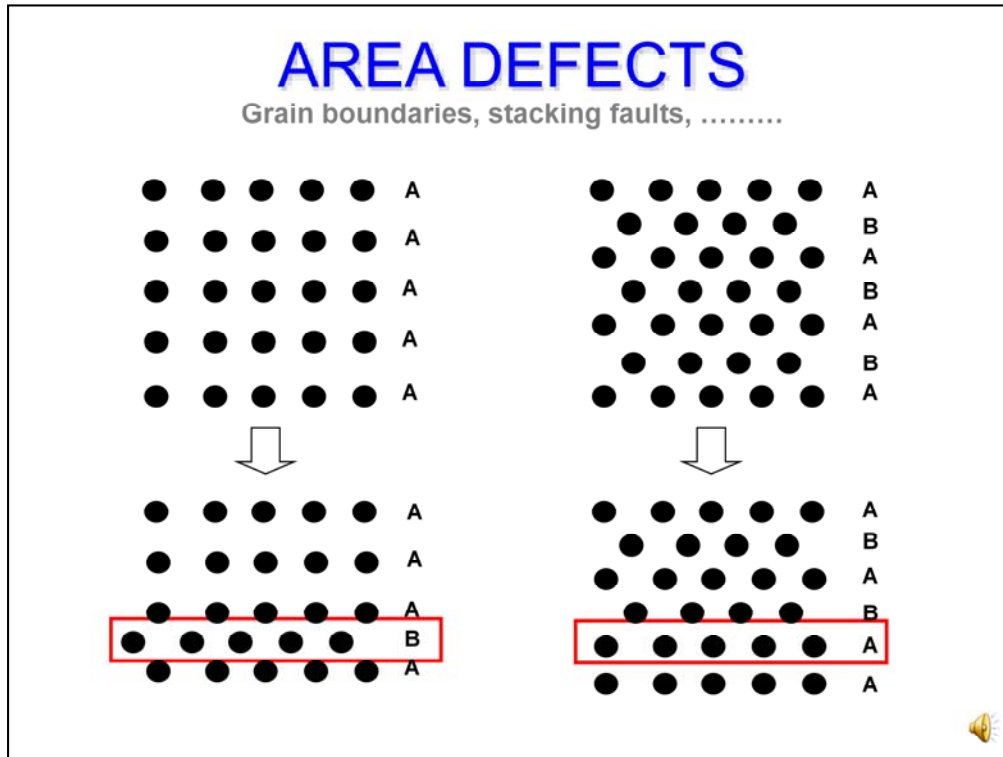
Within a crystal, it is possible to have a missing half plane of atoms. **[CLICK]** When this happens, there is a **DISLOCATION** of the arrangement, but it only causes local disorder around what would be the edge of the missing half plane (a line of disorder). Looking end onto the dislocation, the crystal is perfect above the dislocation and below the dislocation. The edge (or line) is called a **EDGE DISLOCATION**. Instead of the plane being flat, it can be shaped like a screw and produce a **SCREW DISLOCATION** as well.

[CLICK]The important property of a dislocation is that it makes possible very low energy **DEFORMATION** of a crystal. Here is how it works. Under normal circumstances, a perfect crystal could only deform by **[CLICK]** breaking and remaking many bonds at the same time along a plane of shear. **[CLICK]** However, with a dislocation, a line of bonds can be slowly broken and remade **[CLICK] [CLICK] [CLICK] [CLICK]** , causing portions of the crystal to slip or shear over one another. **[CLICK]** Study the sequence for this event. **[PAUSE]**



During solidification, the many centers of growing crystals are formed about the same time. The growing crystals finally run into each other. **[CLICK]** While each crystal may have the same crystalline pattern, at boundaries the internal arrangements are rarely aligned in a way to join together. Therefore, a solid is made up of many crystals and is called polycrystalline. **[CLICK]** Each of the crystals is called a grain. **[CLICK]** During early metallurgical science, low power light microscopy made the crystals look like grains of sand.

Therefore, the boundaries are called **GRAIN BOUNDARIES**. **[CLICK]** These boundaries represent surfaces of disorder or disarrangement between neighboring crystals. If the same solid is formed differently, it could contain different numbers of grains or different size distributions of grains. The number and/or architecture of grain boundaries will affect the properties of the material.



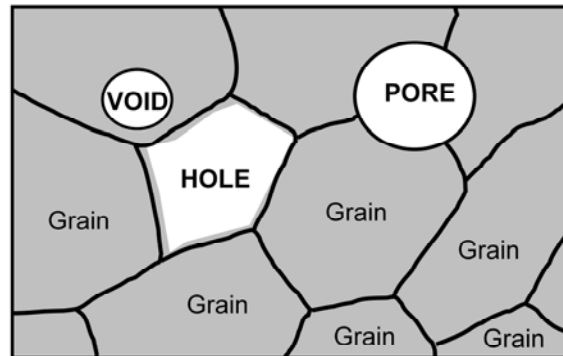
Within a crystal (or grain) the relative alignment of consecutive planes of atoms should be totally symmetrical as shown in the upper left. Each successive layer of atoms should be lined up on top of the previous one to reflect the crystalline pattern. **[CLICK]** For a simple cubic arrangement, we can label each layer as “A” **[CLICK]** since for each layer the atoms are in the same relative positions. The stacking is perfect. **[CLICK]** However, it is possible that one layer could be improperly stacked during formation of the crystal, as shown, **[CLICK]** and this would create a STACKING FAULT.

[CLICK] Consider a more complex arrangement in which the planes alternate in positions **[CLICK]**. If one of the planes were not aligned **[CLICK]** then this would also produce a STACKING FAULT.

There are several other types of area defects as well, but grain boundaries and stacking faults are the most common.

VOLUME DEFECTS

Holes, Pores, ...



Polycrystalline solid



The most prevalent 3-D types of defects are VOIDS, HOLES, and PORES. For all practical effects, all are the same. **[CLICK]** Generally, a VOID forms within a grain. **[CLICK]** HOLES form because grains end up not growing together during solidification. **[CLICK]** A PORE is typically formed by shrinkage or gas formation during solidification and is generally more round in shape. However, all have the same overall effect of dramatically weakening the solid.

More often than not, we refer to all missing material collectively as POROSITY. A general rule is that 10-20% porosity decreases the overall strength by one half. Dental materials contain from 0.5% to 20% porosity. One of the major challenges for all dental materials is to fabricate them without also creating some porosity.

Another type of volume defect is a CRACK. It may form on the surface or from within the interior. If the crack runs between grains it is called INTERGRANULAR. If it runs through grains, it is called TRANSGRANULAR. Cracks are generally considered as volume defects rather than surface defects because there is a large volume of missing material contained between the sides of a crack at some point.

On the surface you may also encounter PITS which are often created by the erosion or corrosion of part of all of a grain.

SUMMARY of DEFECTS

Defects at all levels of microstructure



Now let's see how well you can recognize the different type of defects within the polycrystalline solid above.

Start at the top of the diagram and try to identify VACANCY, SUBSTITUTIONAL, and INTERSTITIAL defects. **[CLICK]**

Next look for a LINE DEFECT in the next grain. **[CLICK]** It is called an EDGE DISLOCATION.

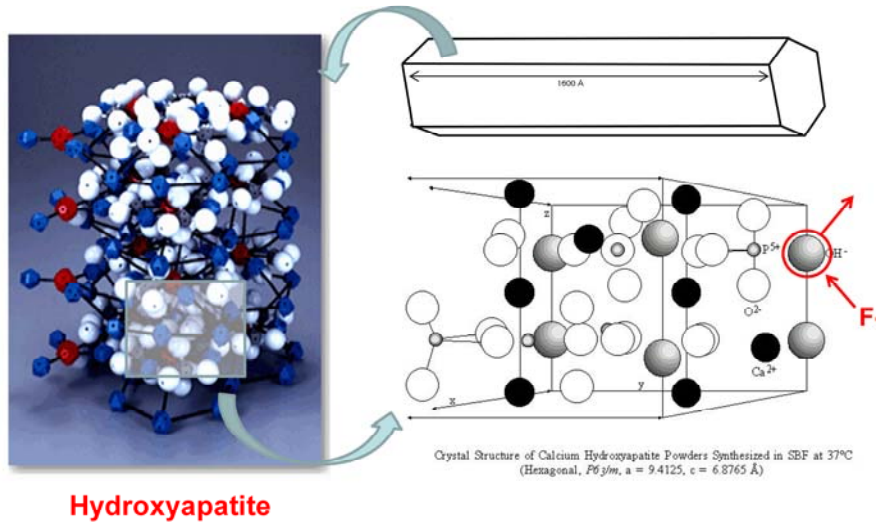
Next look for a 2D defect within the neighboring grain, called a STACKING FAULT **[CLICK]** and the defect along the surfaces of neighboring grains called GRAIN BOUNDARIES. **[CLICK]**

Now try to identify the next defects that appear from the middle to the bottom of the diagram. **[CLICK]** You should see a VOID and HOLE – **[CLICK]** and then a CRACK and PIT.

Study this diagram.

DENTAL APPLICATIONS

Examples of why this is important – F ion substituted hydroapatite



Why is all of this information important? Let's consider some an example of how these sorts of things are important.

Hydroxyapatite (or HA) crystals within enamel are dissolved in acid that is produced and concentrated under dental plaques. We would like to slow down or stop this process. One interesting and very effective way is to remove some of the hydroxyl ions (OH^-) in the $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ lattice **[CLICK]** and substitute them with fluoride ions (F^-). You do not have to replace many ions at all -- only about 0.1% (one per thousand) -- to get a very positive "anticaries" effect. This very small distortion of the lattice makes the lattice more acid resistant and thus prevents the destruction from dental caries. We refer to the new lattice as "fluoride-ion substituted hydroxyapatite." It is 99.9% still HA. If you replaced all the ions, you would actually create fluorapatite, or FA.

QUICK REVIEW

Defects.

- **What is an example of a “zero dimensional” defect?**
VACANCY, SUBSTITUTIONAL, INTERSTITIAL
- **Which “line defect” is primarily responsible for deformation?**
DISLOCATION
- **What are 2 types of “area defects?”**
GRAIN BOUNDARIES, STACKING FAULTS
- **What is a “volume defect” other than a hole, void, or pore?**
CRACK or PIT.
- **What determines the number of original defects?**
TIME AND TEMPERATURE CONDITIONS DURING FABRICATION.



Here is a quick review of the concepts from this module.

[CLICK] (1) **What is an example of a zero dimensional defect?**

[CLICK]

[CLICK] (2) **Which line defect is primarily responsible for deformation?**

[CLICK]

[CLICK] (3) **What are 2 types of area defects?**

[CLICK]

[CLICK] (4) **What is a volume defect other than a hole, void, or pore?**

[CLICK]

[CLICK] (5) **What determines the number of original defects?**

[CLICK]



THANK YOU



THANK YOU.