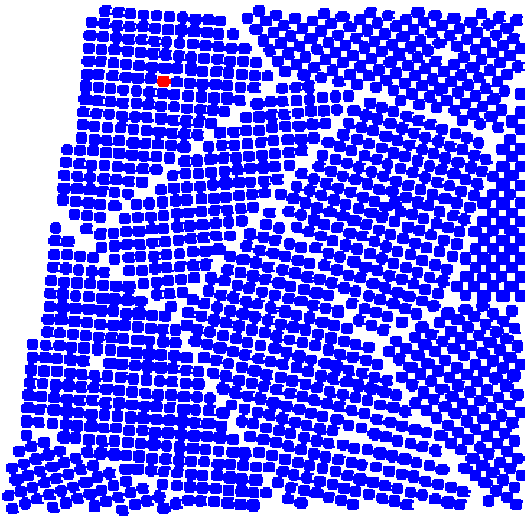A two-dimensional representation of a perfect single crystal with regular arrangement of atoms. But … nothing is perfect, and structures of real materials can be better represented by the schematic drawing below.

Schematic drawing of a poly-crystal with many defects. We can see several grains of the crystal separated by boundaries, a few missing and extra atoms, as well as an interrupted raw of atoms. Figures by Helmut Föll, University of Kiel, Germany

Real crystals are never perfect, there are always defects.

"*Crystals are like people, it is the defects in them which tend to make them interesting!*" - Colin Humphreys.

Introduction

You have been introduced to the lattice structures and types of bonding in crystalline solids in earlier lectures. You know that the behavior of electrons determine the way the atoms interact - the type of bonding (metallic, ionic, covalent, and van der Waals) that holds atoms in a solid together. But is the knowledge of bonding and crystal structure sufficient to predict the macroscopic properties of materials?

In this lecture we will discuss different types of imperfections or **defects** in the ideal arrangement of atoms in a crystal. We will see that the presence of a relatively small number of **defects have a profound impact on the macroscopic properties of materials**, and the control (and intentional introduction) of defects is important in many kinds of material processing.

Examples of the relevance of defects in crystals for life in general or materials science in particular: When/if you buy a diamond ring, it is mostly the number and type of defects in the diamond crystal that define the amount of money you pay for a given crystal size. It is generation, accumulation, and interaction of defects in different parts of your car that define the mileage on your car when you tow it to the junk-yard. Production of advanced semiconductor devices require not only a rather perfect Si crystal as starting material, but also involve introduction of specific defects in small areas of the sample. Forging a metal tool introduces defects … and increases strength and elasticity of the tool. Note, that in this case the required properties are achieved without changes in composition of the material, but just by manipulating the crystal defects.

In this lecture we will discuss the three basic classes of defects in crystals:
- **Point defects** - atoms missing or in irregular places in the lattice (lattice vacancies, substitutional and interstitial impurities, self-interstitials).
- **Linear defects** - groups of atoms in irregular positions (e.g. screw and edge dislocations).
- **Planar defects** – the interfaces between homogeneous regions of the material (grain boundaries, stacking faults, external surfaces).

We will also consider examples of interaction among the defects of different types and their relation to the properties of material, (only examples, not a systematic discussion).
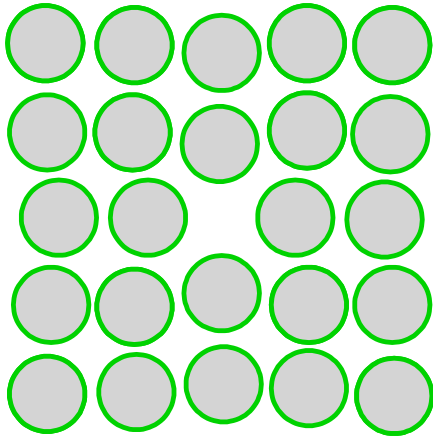
Schematic representation of vacancy in a two-dimensional crystal.
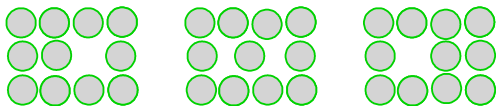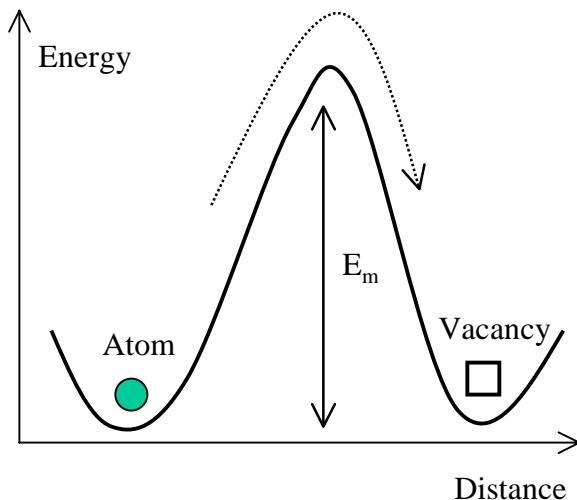
Schematic representation of the diffusion of an atom from its original position into a vacant lattice site. At activation energy E_m has to be supplied to the atom so that it could break inter-atomic bonds and to move into the new position.

Point Defects: Vacancies

A perfect crystal with regular arrangement of atoms can not exist. There are always defects, and the most common defects are point defects. This is especially true at high temperatures when atoms are frequently and randomly change their positions leaving behind empty lattice sites, called **vacancies**. In most cases diffusion (mass transport by atomic motion) - can only occur because of vacancies.

How many vacancies are there? The higher is the temperature, more often atoms are jumping from one equilibrium position to another and larger number of vacancies can be found in a crystal. Actually, the number of vacancies, N_v, increases exponentially with the absolute temperature, T, and can be estimated using the equation (Boltzmann Distribution):

$$N_v = N_s \exp\left(-\frac{E_v}{k_B T}\right)$$

where N_s is the number of regular lattice sites, k is the Boltzmann constant, and E_v is the energy needed to form a vacant lattice site in a perfect crystal. Using this simple equation we can estimate that at room temperature in copper there is one vacancy pet 10^{15} lattice atoms, whereas at high temperature, just below the melting point there is one vacancy for every 10,000 atoms. These are the lower end estimations, a large numbers of additional vacancies can be introduced in a growth process or as a result of further treatment (plastic deformation, quenching from high temperature to the ambient one, etc.).

How often do vacancies jump? In order for atom to jump into a vacancy site, it needs to posses enough energy (for example, thermal energy) to squeeze through its neighbors. The energy necessary for motion, E_m, is called *the activation energy for vacancy motion*. The average thermal energy of an atom is usually much smaller that the activation energy E_m and a large fluctuation in energy (when the energy is "pooled together" in a small volume) is needed for a jump. The probability of such fluctuation or frequency of jumps, R_j, depends exponentially from temperature and can be described by equation that is attributed to Swedish chemist Arrhenius :

$$R_j = R_0 \exp\left(-\frac{E_m}{k_B T}\right)$$

where R_0 is an attempt frequency proportional to the frequency of atomic vibrations.
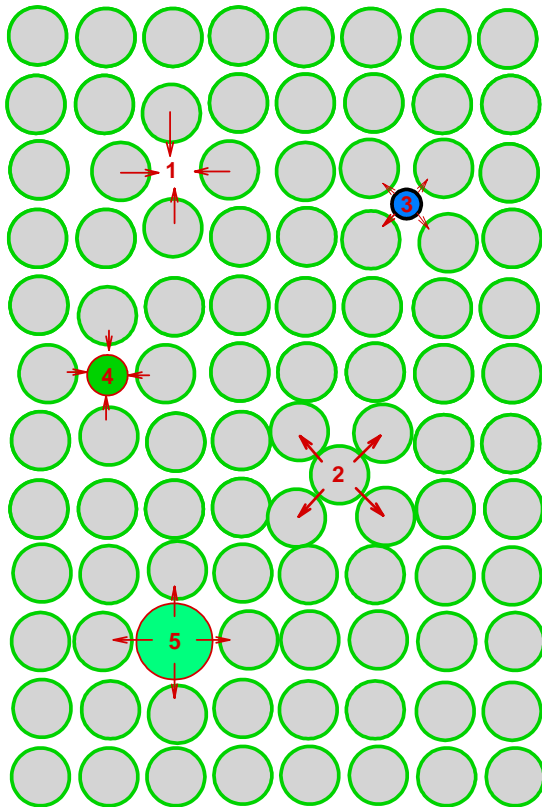
Schematic representation of different point defects in a crystal. (1) vacancy; (2) self-interstitial; (3) interstitial impurity; (4), (5) substitutional impurities. The arrows show the local stresses introduced by the point defects.
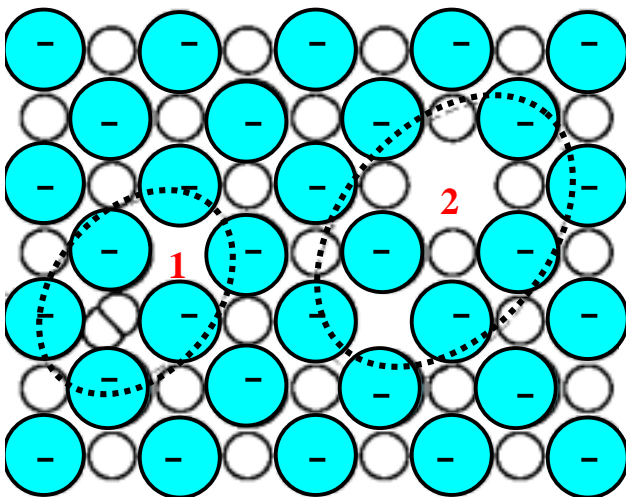
Schematic representation of (1) Frenkel defect (vacancy-interstitial pair) and (2) Schottky defect (a pair of cation and anion vacancies) in an ionic crystal.

More on Point Defects

Interstitials – atoms that are squeezed in between regular lattice sites. If the interstitial atom is of the same species as the lattice atoms, it is called **self-interstitial**. Creation of a self-interstitial causes a substantial distortions in the surrounding lattice and costs more energy as compared to the energy for creation of a vacancy ($E_i > E_V$) and, under equilibrium conditions, self-interstitials are present in lower concentrations than vacancies (see the Arhenius equation in previous page). Foreign, usually smaller atoms (carbon, nitrogen, hydrogen, oxygen) are called **interstitial impurities.** They introduce less distortion to the lattice and are more common in real materials and more mobile. If the foreign atom atom replaces or substitutes for a matrix atom, it is called a **substitutional impurity**.

As shown in the schematic drawing, all point defects introduce local distortions to the lattice, and due to these distortions they can feel each other (interact) and feel external stresses. The external stresses or stresses from a larger defects that we will consider next can give a directionality to an otherwise random jumps of atoms. In particular, a pressure gradient result in a flux of vacancies in the direction towards a compressed region of the sample.

In ionic crystals (e.g. table salt – Na^+Cl^-) the bonding is provided by coulombic forces between positively and negatively charged ions. Point defects in ionic crystals are charged as well. The Coulombic forces are very large and any charge imbalance has a very strong tendency to balance itself. To maintain charge neutrality several point defects can be created. A **Frenkel defect** is a pair of cation (positive ion) vacancy and a cation interstitial. Or it may also be an anion (negative ion) vacancy and anion interstitial. However anions are much larger than cations and it is not easy for an anion interstitial to form. A **Schottky defect** is a pair of anion and cation vacancies. In both Frenkel and Schottky defects, the pair of point defects stay near each other because of strong coulombic attraction of their opposite charges.

As will be discussed in lecture on conductors, insulators and semiconductors, some impurities in semiconductors can lead to transistor properties.
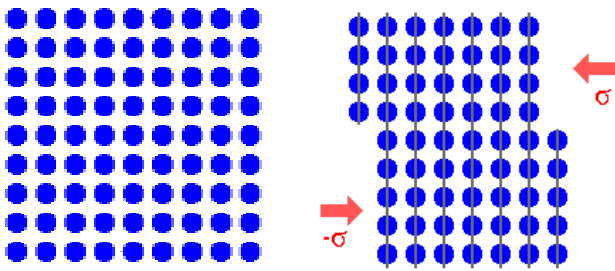
Plastic deformation – the force to break all bonds in the slip plane is much higher than the force needed to cause the deformation. Why?
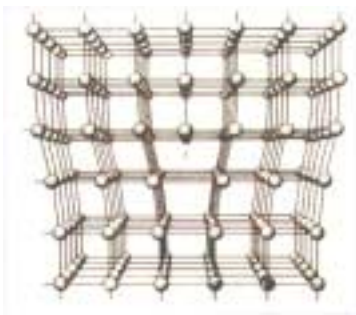

This 3D picture shows the inserted half-plane – dislocation line goes through the center of the picture.

Dislocations

The smelting and forging of metals marks the beginning of civilization. Trial and error over this period of time lead to an astonishing degree of perfection, as can be seen all around us and in many museums. But why metals could be plastically deformed and why the plastic deformation properties could be changed to a very large degree by forging without changing the chemical composition, was a mystery for thousands of years. This became even bigger mystery when in the early 1900's scientists estimated that metals undergo plastic deformation at forces much smaller than the theoretical strength of the forces that are holding the metal atoms together.

The explanation came in 1934 when Taylor, Orowan and Polyani discovered the dislocation. Dislocations can be introduced and thought of as extra lattice planes inserted in the crystal, but not extending through all of the crystal but ending in the dislocation line.

Motion of dislocations allows slip – plastic deformation when interatomic bonds are fractured and reformed. Actually, slip always occurs through dislocations motion.
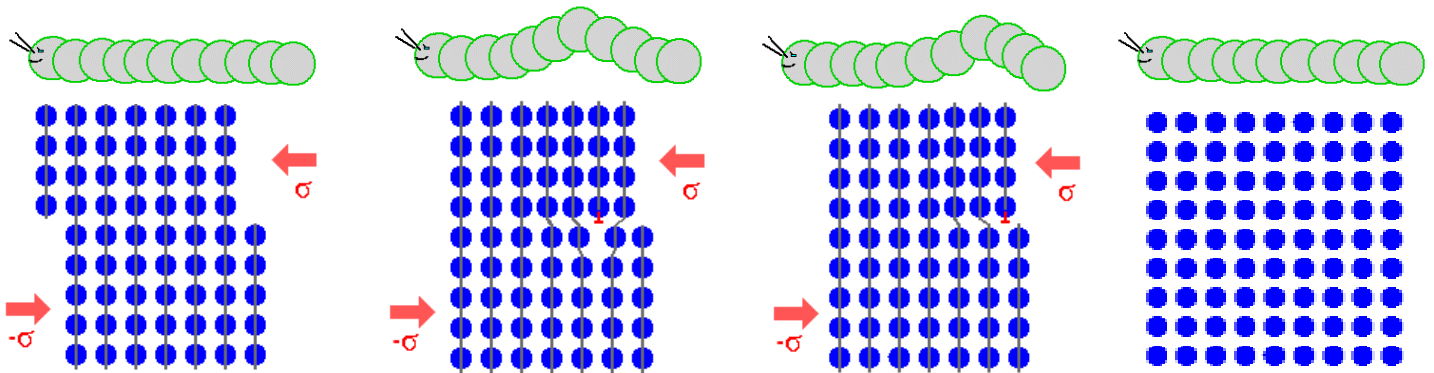

Looking at this diagram we understand why dislocations allow slip at much lower stress than in a perfect crystal. If the top half of the crystal is slipping one plane at a time then only a small fraction of the bonds are broken at any given time and this would require a much smaller force. In the process of slipping one plane at a time a dislocation is created and propagates across the crystal. The propagation of one dislocation across the plane causes the top half of the crystal to move with respect to the bottom half but we do not have to break all the bonds across the middle plane simultaneously (which would require a very large force).

Dislocation motion is analogous to movement of a caterpillar. The caterpillar would have to exert a large force to move its entire body at once. Instead the rear moves forward a bit and creates a hump. The hump then propagates along the caterpillar and moves the caterpillar by a small amount. The same trick may be used to move a large carpet. Instead of dragging the entire carpet one can create a hump in the carpet and then push it across the floor.
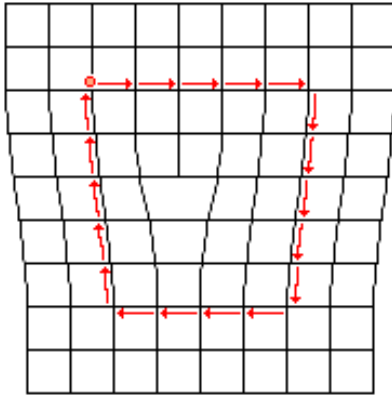
This picture shows how to find the Burgers vector of an edge dislocation.
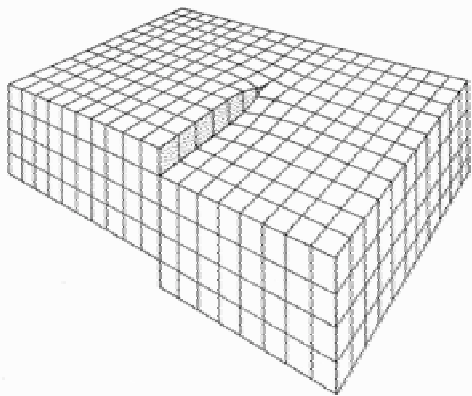
This picture helps to find the Burgers vector of a screw dislocation. It is obvious how a screw dislocation got its name.
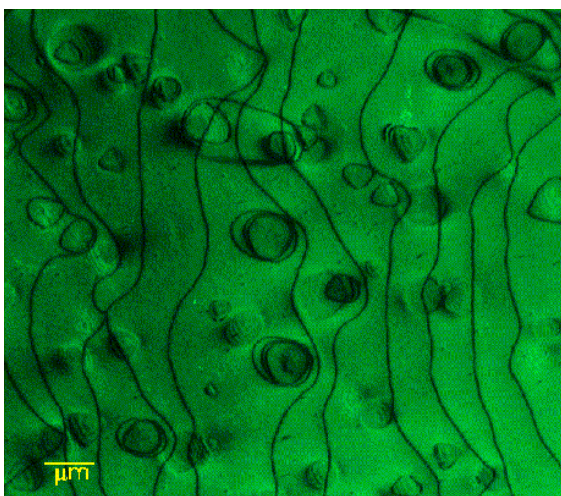
Dislocations in Nickel (the dark lines and loops), transmission electron microscopy image, Manchester Materials Science Center.

More about Dislocations

Dislocations are line-defects: the interatomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. This area is called the **dislocation core**. Dislocations also create small elastic deformations of the lattice at large distances.

To describe the size and the direction of the main lattice distortion caused by a dislocation we should introduce so-called **Burgers vector b**. To find the Burgers vector, we should make a circuit from from atom to atom counting the same number of atomic distances in all directions. If the circuit encloses a dislocation it will not close. The vector that closes the loop is the Burgers vector **b**.

Dislocations that have been considered until now have Burgers vector directed perpendicular to the dislocation line. These dislocations are called **edge dislocations**. There is a second basic type of dislocation, called **screw dislocation**. The screw dislocation is parallel to the direction in which the crystal is being displaced (Burgers vector is parallel to the dislocation line).

The exact structure of dislocations in real crystals is usually more complicated than the ones shown in this pages. Edge and screw dislocations are just extreme forms of the possible dislocation structures and even they usually would be split in "partial" dislocations. Partial dislocations have their cores spread out over a larger area and look much more complicated.

The dislocations move along the densest planes in the densest directions, because the stress needed to move the dislocation increases with the length of the Burgers vector and the spacing between the planes. There are many such dense planes in FCC and BCC metals, so these materials have **high ductility**, meaning that they deform a great deal before they break. Metals are strengthened by making it more difficult to move dislocations (to increase strength we have to introduce obstacles to dislocation motion, e.g. interstitial atoms).

In ionically bonded materials the Burgers vector is very long because the ion must move past a repulsive site to the next location of the same charge, so slip is difficult and the materials are **brittle**. Likewise, the low density packing of covalent materials makes them brittle because there are no dense planes for dislocation movement.
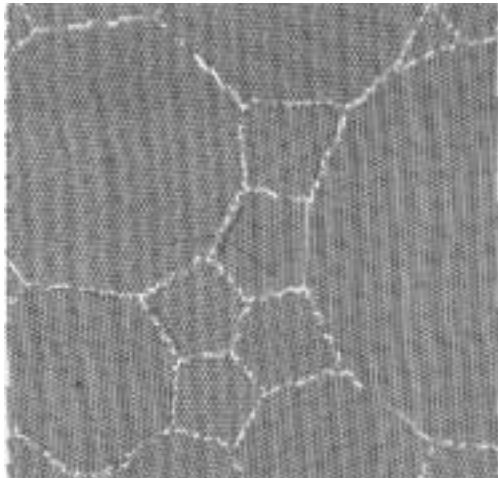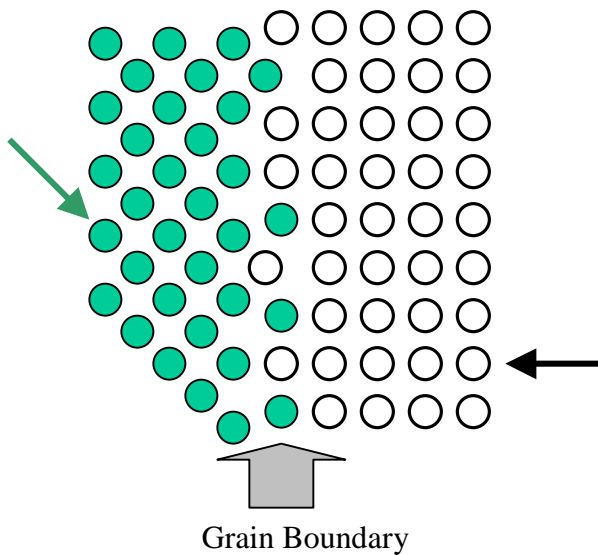
Grain Boundary

Atomistic model of a nanocrystalline solid
by Mo Li, JHU
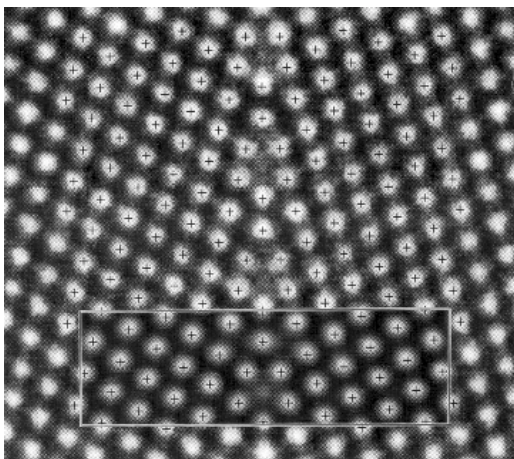
High-resolution Transmission Electron
Microscope image of a tilt grain boundary in
aluminum, Sandia National Lab.

Planar defects. Grain Boundaries. Polycrystals

Until now we considered structure and defects of *single crystals* that have periodic, regular atomic arrangement throughout the sample. Single crystals, however, can be rarely found in real materials unless the growth conditions are specially designed and controlled, as, for example, when producing silicon single crystals for microelectronic devices or blades for turbine engines made of superalloys. Instead, solids generally consist of a number of small crystallites or *grains*. The grains can be from nanometers to millimeters in size and the orientations of atomic planes are rotated with respect to the neighboring grains. These materials are called **polycrystals**. The individual grains are separated by **grain boundaries**, regions of are less densely and regularly packed as compared to the bulk of the grains.

We can distinguish between small-angle grain boundaries and large-angle grain boundaries. It is possible to describe small angle grain boundaries as an array of dislocations. This is a transmission electron microscope image of a small angle tilt boundary in Si. The red lines mark the edge dislocations, the blue lines indicate the tilt angle.
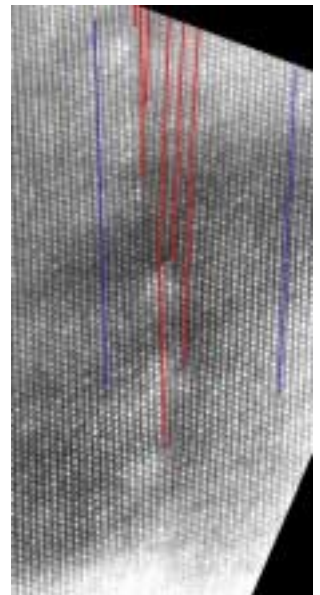
Another type of surface defect within lattices is a **stacking fault** where the sequence of atom planes has an error.


Twin boundaries are similar, and may be produced by deformation of materials. This gives rise to **shape memory metals**, which can recover their original shape if heated to a high temperature. Shape-memory alloys are twinned and when deformed they untwin. At high temperature the alloy returns back to the original twin configuration and restore the original shape.
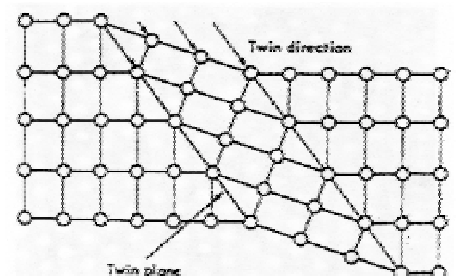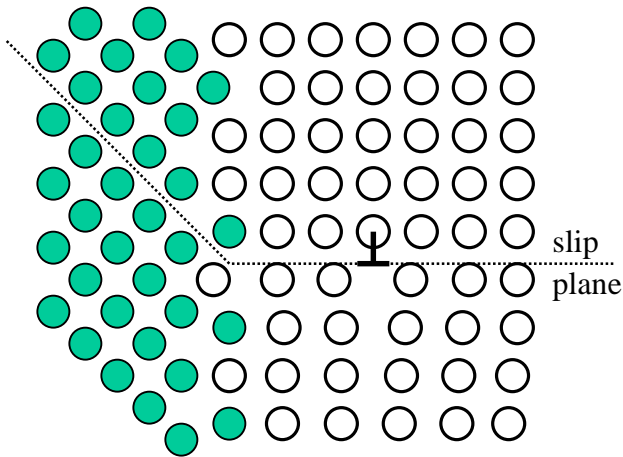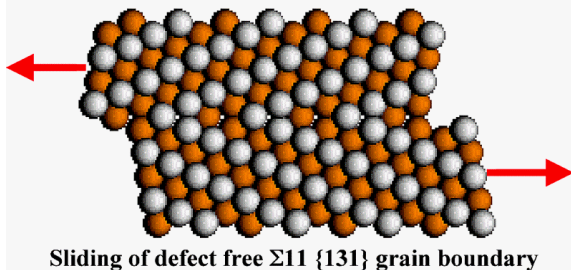
Grain boundary barrier to dislocation motion: slip plane discontinues or change orientation.
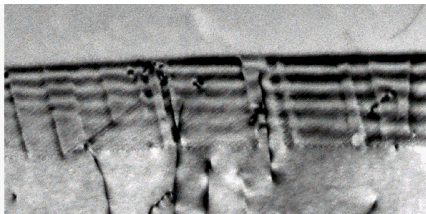
Extrinsic grain boundary dislocations in Al

Sliding of defect free Σ11 {131} grain boundary

Superplastic deformation of aluminum. To understand the micro-mechanisms of superplastic deformation one needs to know the force or stress required to slide the aluminum along a grain boundary. The force can not be measured experimentally and computer simulations are used to get insight into this invaluable material property.

Grain Boundaries – Polycrystalline materials

Grain boundaries are important in several ways. They present paths for atoms to diffuse into the material and scatter light passing through transparent materials to make them opaque. They also affect mechanical properties. The boundaries limit the lengths and motions of dislocations that can move. This means that smaller grains (more grain boundary surface area) strengthens materials.

The size of the grains can be controlled by the cooling rate when the sample is produced from the melt. Generally, rapid cooling produces smaller grains whereas slow cooling result in larger grains. At room temperature large grains generally result in low strength, hardness and ductility.

Any defect in the regular lattice of a material disrupts the motion of dislocation, also described as making slip more difficult. This includes the point defects and surface defects mentioned above, and also other dislocations. The motion of dislocations produces more dislocations, which impede the motion of other dislocations and increase the force needed to move then (strengthening the material).

Slip of grains past either other occurs at high temperatures and can lead to superplastic deformation. Superplastic deformation involves low-stress sliding along grain boundaries.
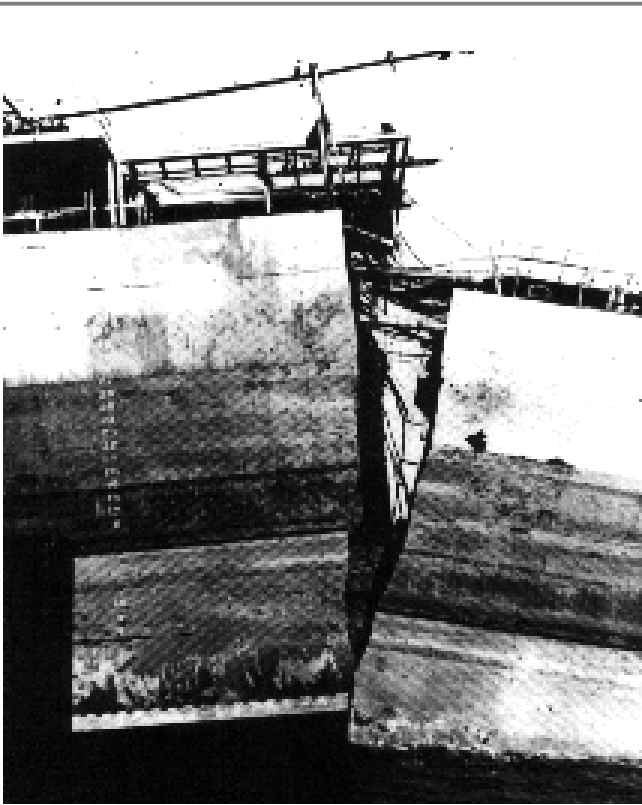
Brittle fracture of a Liberty ship.

Crack   Dislocations
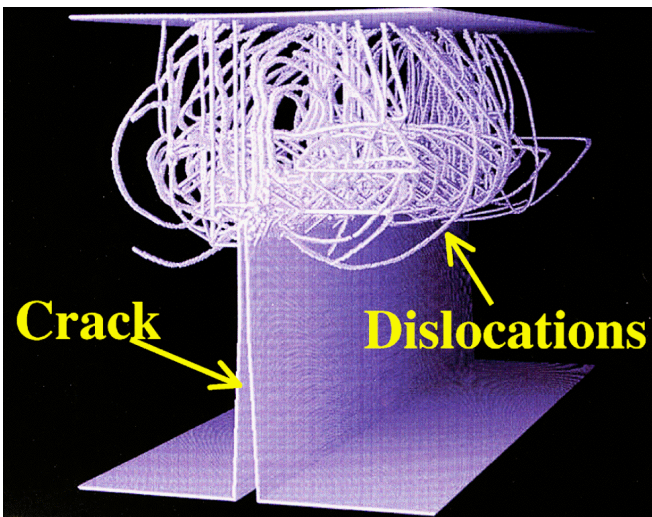
V. Bulatov et al., Molecular dynamics
simulation of crack propagation.
Nature 391, #6668, 669 (1998)

Defects in plastic deformation and fracture

Elastic deformation - is temporary (reversible), involves bond stretching. **Plastic deformation** is permanent (irreversible), involves defects formation and movement.

Strengthening – the ability to plastically deform depends on the ability of dislocations to move. Therefore, to increase strength one have to impede dislocation motion. This can be done by introducing defects: point defects (alloying), dislocations (work hardening), making smaller grains (e.g. by fast cooling from the melt).

Low temperatures can severely embrittle steels. The Liberty ships, produced in great numbers during the Second World War were the first all-welded ships. A significant number of ships failed by catastrophic fracture. Fatigue cracks nucleated at the corners of square hatches and propagated rapidly by brittle fracture. In earlier ships, the riveted plates acted as natural crack arresters. These were absent in the all-welded Liberty ships. The problem was solved by improvements in ship design and steel quality.

This atomic-level simulation illustrates some of the complex events that occur as a crack moves in a ductile metal. At first, the crack moves very rapidly and local bonds break in a "brittle" manner, but at some point the crack-tip begins to emit dislocations (the tangles in the picture) and stops propagating. Such a crack is said to become blunted and begins to cause intense local deformation but not failure. Cracks that can emit dislocations usually stop before complete structural failure occurs. However, when the material is unable to emit dislocations, crack propagation does not terminate, which eventually leads to failure and irreversible damage of the material. The fundamental phenomena that determine whether a material is able to emit the beneficial dislocations are yet to be elucidated.

In general, there are many open questions on the behavior, properties and interaction of defects in crystals. This an area of active current experimental and theoretical research.