

416 – Solid State Physics

8-29-2016; Introduction & Overview

Assignment: **Read chapter 1 of Kittel** for next time on crystal symmetries.

This course covers concepts in solid state physics. Note that physics-related solids research is usually called condensed matter physics, which includes superfluids, quantum fluids, biological matter, and other topics not just including solids. Many body physics refers to studies of interacting particle systems that occur in solids (but also for example in nuclear matter). On the other hand, materials physics is a term used for research in new materials, and normally implies a connection to technological applications, and device physics normally refers specifically to semiconductor devices and some of the underlying solid state physics. Our course will cover some of the fundamental concepts in solids physics, particularly crystal lattice structures, electron bands, and phonon behavior, and will also include some discussion of practical applications and current research topics.

We start with some of the ways solids can be classified:

(1) Atomic-scale structures

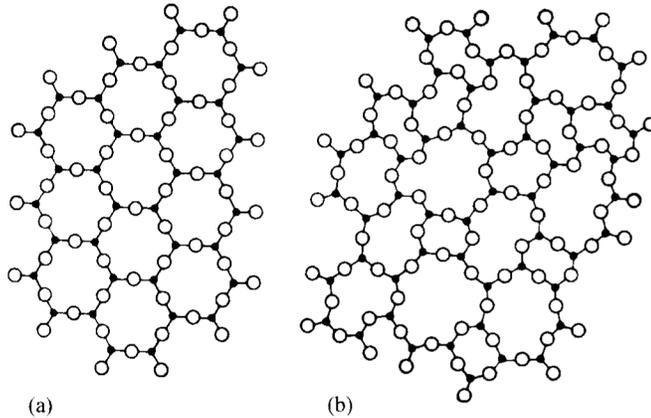
Most of this course deals with crystals. Historically, the physics of ideal crystalline materials laid the foundation for understanding of electronic properties of materials, and led to important developments in metals and alloys, and semiconductors for transistors and other devices. Crystals continue to provide the framework for the study of many other condensed matter systems, while the physics of periodic crystals also find applications in information science, imaging, and other areas removed from solid state systems.

Crystals in solids feature regular arrays of atoms. See the schematic figure on the next page contrasting the regular structure of quartz to a glassy structure ("glass") formed from the same material, SiO_2 . For most such solids the crystal state is the ground state; crystals have low entropy and thus are typically the low-temperature equilibrium state. For example metals, ice, inorganic materials such as NaCl , and small organic molecules will typically form crystals. Even purified macromolecules such as proteins typically have crystalline lowest-energy states; sometimes great effort is placed into growing such crystals to identify their molecular arrangement (using x-ray crystallography; see chapter 2).

By contrast a *glass*, or amorphous material, is a disordered array. Besides window glass, many polymers easily form glassy structures. "Metallic glasses" can also be formed with special processing techniques, usually rapid quenching from the melt or high-energy mechanical processing. (In fact materials which form as bulk metallic glasses in mm-cm sizes are currently of great interest, driven by demands for new structural materials.) Glasses have no long-range order, although often some *short-range order* is observed.

Other types of structures include *liquid crystals*, which exhibit partial order, for example crystal-like order in one direction only, or an ordering of the molecule orientations without any regularity to the molecular positions. Further examples of types of structural order include

quasicrystals and *incommensurate materials*. The discovery of quasicrystals was the subject of a recent chemistry Nobel Prize; such materials have interesting physical properties, and can be considered to correspond to two or three-dimensional Penrose tilings. (A two-dimensional Penrose tiling can be seen in the atrium of our MIST institute building.)



from *Glasses for Photonics*,
Yamane and Asahari,
Cambridge Univ. Press
2000

Fig. 1.1. Schematic two-dimensional illustration of the atomic arrangement in (a) crystal and (b) glass [2].

(2) Electrical conductivity.

Metal vs. Insulator is one of the essential features distinguishing materials. The table below shows the four categories that are usually defined. Electrical resistivities cover many orders of magnitude, and the specific dividing line between neighboring categories is actually somewhat arbitrary. Also shown is the typical temperature dependence (often used as a simple way to identify metals from insulators), and the more fundamental definition in terms of the electron bandgap and the electrical carriers. This classification works for simple materials (e.g. those for which electron-electron interactions are not so strong as to make the band-structure approximation work poorly).

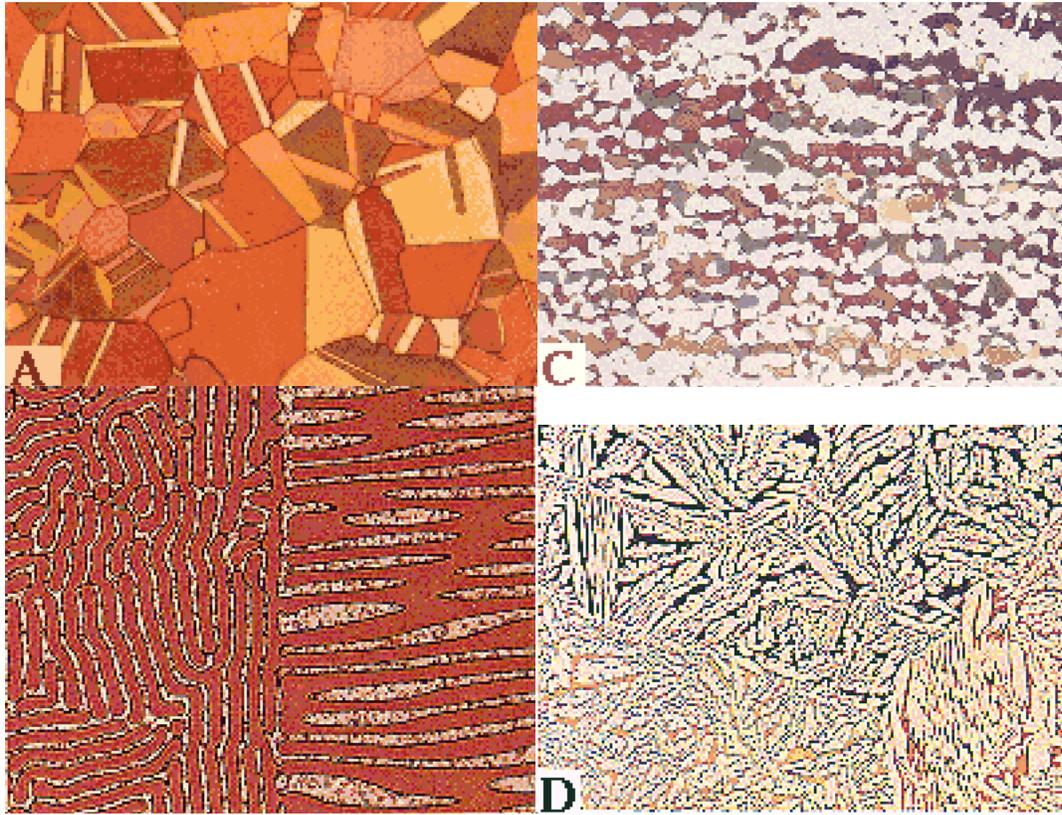
	approx. range of resistivity (ρ)	Change of resistivity with T	bandgap (& charge carrier properties)	bonding
Metal e.g. copper	10^{-5} to 10^{-7} Ω -cm	increases with T	no gap ("electron gas")	weak (metallic)
Semimetal e.g. bismuth	10^{-3} Ω -cm	increases with T	no gap (small band overlap; low-density electron gas)	
Semi-conductor e.g. silicon	10^{-2} to 10^{+9} Ω -cm	decreases with T	small gap (no carriers at $T = 0$, carriers introduced thermally or by impurities)	
Insulator e.g. diamond	10^{14} to 10^{22} Ω -cm	decreases with T	large gap; (transport may be surface-dominated/irreproducible)	strong*

* Simple insulators have strong ionic or covalent bonds, and as a result can be hard, although typically brittle. However not all insulators behave this way; molecular solids (many organic materials) have covalently bonded molecules joined by van der Waals bonds, and are more typically soft. There are also van-der-Waals atomic crystals (solid noble gases).

(3) Grain sizes, and length-scale issues for physical properties:

Large *Single Crystals* occur rarely in nature, but are grown for special purposes, notably silicon wafers for electronic devices, which based on rather amazing technical advances are cut from 2 meter-long, essentially perfect crystals.

More typical materials contain a collection of internal crystal grains arranged in a pseudo-random way. Often the crystal nature is not readily apparent; optical micrographs showing the hidden crystal structure in brass alloys (Cu-Zn) are shown below:



The grains can be seen after etching, and represent individual crystals. Crystallite sizes range from a few μm to more than $100 \mu\text{m}$. Reference: www.metallography.com/types.htm.

So when is a crystal a crystal? In other words, at what scale do small crystallites behave the same as infinitely large crystals? The answer depends greatly on what type of property we are interested in.

(a) Mechanical properties are highly dependent on defects and the motion of dislocations. These depend crucially on macroscopic structures such as seen above. Roughly speaking, a solid made of crystallites and having many dislocations or including grains of a different phase can be much stronger than a single crystal (because the interfaces and disorder pin dislocations – see chapter 21 in Kittel). Thus the different materials in the four pictures above would have significantly different strengths, even for grain sizes of 10s of μm (10^{13} atoms). For mechanical properties it is thus important to know the structure on many length scales including rather large. However often the relevant grain sizes may be very small. Also note that in some cases specially

prepared nanostructured materials may be mechanically very strong (“superhard”) because of the very large density of dislocation-pinning disorder.

(b) Electronic structure: When metal crystals become very small, the *bandstructure* approximation breaks down. However, this requires *very small* length-scales of order 10 nm (10^3 atoms), and can also be called the electronic size effect. In semiconductor systems, when the size effect is used to generate specific properties this is a form of bandgap engineering, and our ability to control materials on the nano-scale has led to the explosion of research in nano-technology.

(c) Electrical transport: For example consider electrical resistivity, which was included the table above. Resistivity is due to electrons in crystals scattering randomly, and the scattering length is called the mean free path. In perfect specimens at low temperatures the mean free path may be as much as 100 μm , or even mm sizes, and may be due to scattering by lattice vibrations (phonons), or by (rare) collisions with other electrons. In the particular case of specialized *two-dimensional electron gas* semiconductor-based devices, quantum hall effects and other quantum phenomena can be observed at low temperatures associated with the coherent behavior of the electrons. However, at typical temperatures scattering is much stronger, with mean free paths less than 1 μm . Beyond this size, crystal grains will behave much as if they were infinite-size crystals (for example the micrographs pictured above would be in this category; the conductivity may depend almost entirely on the purity inside each grain). However, sometimes grain boundaries themselves may scatter strongly, significantly reducing the electrical conductivity.

(d) Magnetism: There are several relevant length scales for magnetic materials, however in general these are less than 1 μm , so it is not until nano-sizes are reached that the grain size has great significance for the magnetic properties.

As for point *b* above, here is some more detail on band formation in tiny crystals: Omar’s book gives a schematic of the electron bands in lithium, as an example:

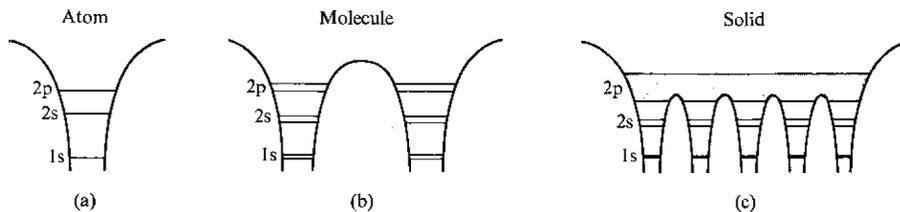


Fig. 5.1 The evolution of the energy spectrum of Li from an atom (a), to a molecule (b), to a solid (c).

The point is that overlap of discrete electronic levels leads, for the large-crystal approximation, to smeared-out bands of electron states (the shading of bands in the figure on the right may not show clearly in the scan). Note however that for typical materials these bands don’t maintain pure-*s* or pure-*p* characteristics in the metal as in the picture. Here is a figure from the book by Mott and Jones providing a more accurate picture (the overlapping bands are mixed):

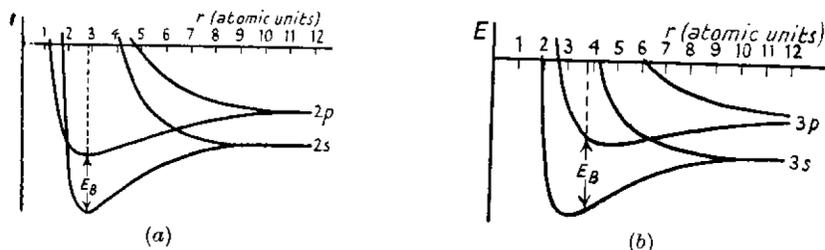
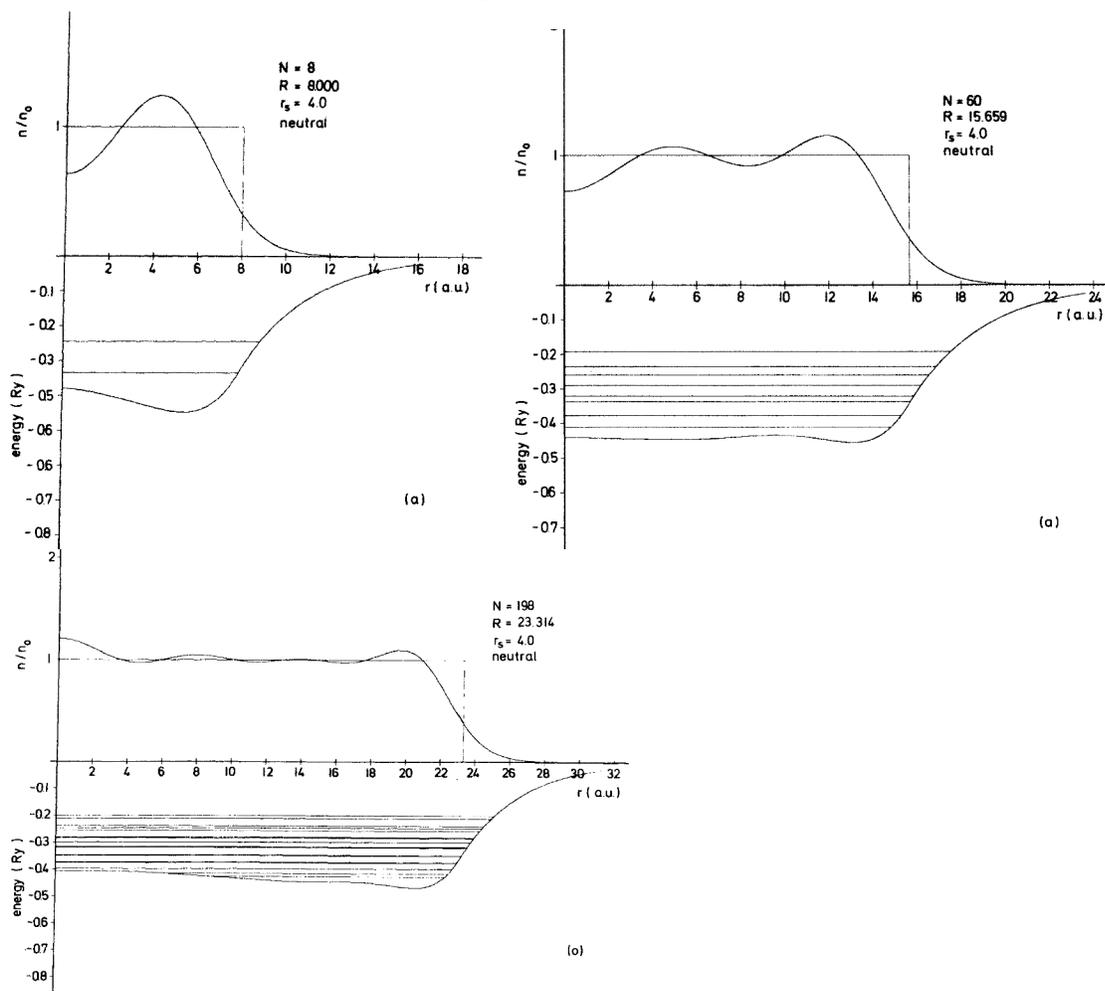


FIG. 36. Energies of states in crystal lattices; (a) lithium, (b) sodium.

An illustration of the formation of bands in small clusters is provided by the following figures from W. Ekardt, Phys. Rev. B **29**, 1558 (84). The figures show data calculated (in a rather simple "jellium" model) for sodium clusters with 8, 60, and 198 electrons respectively. [The curves indicate charge density and effective potential, while horizontal lines are electron energy levels.]



In this example, even for 198 electrons, the "band" has started to fill in. This cluster corresponds roughly to a $6 \times 6 \times 6$ -atom cluster, and its diameter is about 0.2 nm. Most of its atoms are at the surface. This shows that one really must go to nano-scale particles before the *infinite-crystal approximation* runs into serious trouble for ground-state electronic calculations.

Crystals: Basic quantities *Reading: Ch. 1 of your text.*

(1) Crystal = Bravais lattice + Basis

Bravais lattice: means a repeated set of mathematical points generated in the following way:

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3, \quad \text{where the } n_i \text{ cover all integers}$$

$\{\vec{R}\}$ is the set of “Lattice Vectors;” these define the cells in which the atoms reside

The Basis is the set of constituents (atoms, etc.) which are repeated once per Lattice Vector to make up the entire crystal. Generally we will use the notation \vec{d} for the basis set, locating the basis atoms starting at the Bravais points. Thus the atom locations become $\vec{r} = \vec{R}_i + \vec{d}_j$.

Note, in solids an atom does not *have* to be located on each Bravais lattice point: for simpler structures usually it is easiest to have one of the atoms form the "corners" of the cell. However it is always possible to re-define the basis set so that none of the atoms is located at (0,0,0).

(2) Primitive Lattice Vectors:

These are the $\vec{a}_1, \vec{a}_2, \vec{a}_3$ defined above, used to construct the complete set of Lattice Vectors (i.e. $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$). For a given lattice, the Primitive Lattice Vectors are *not* unique; there are an infinite number of possible choices.

(3) Primitive cell

This is a space region, when translated by all the lattice vectors \vec{R} , will fill all space once over, with no gaps or overlaps. Each cell can be associated one-to-one with a unique Bravais lattice point, which will often (but not always) be located at a corner.

Like the lattice vectors, the primitive cell is not unique for a given lattice, however its volume is unique: $V = \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3$, no matter which primitive vectors are chosen. (In 2 D, the result is:

$$V = |\vec{a}_2 \times \vec{a}_3| \cdot \vec{a}_1)$$

You can always construct a primitive cell as the *parallelepiped* having three edges consisting of three Primitive Lattice Vectors. But that is not the only way – for example the Wigner Seitz cell is not such a cell.

(4) Wigner Seitz primitive cell is defined as:

The space region defined as being closer to a given Lattice Point than any other Lattice Point.

(This is an important concept mostly because in Reciprocal Space the Brillouin Zones are defined in an analogous way. We will see those ideas later – see ch. 2.)

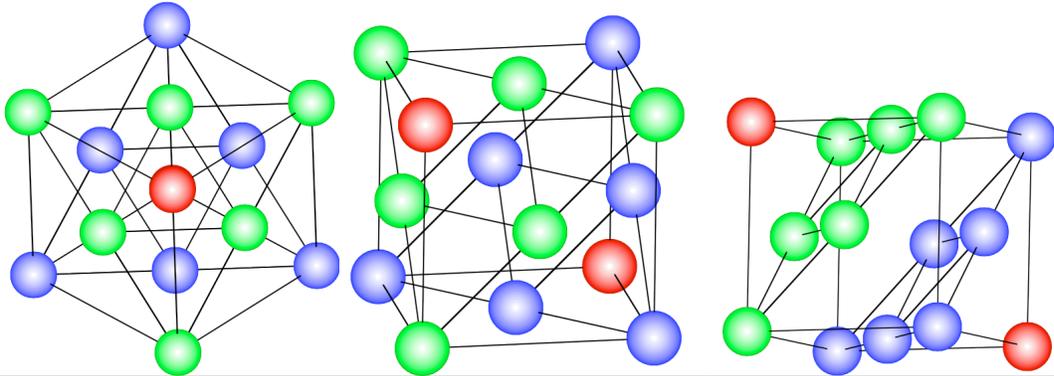
(5) Conventional cell:

The conventional is a cell larger than the primitive cell, which still tiles space and can generate a given crystal. It is normally chosen to show crystal symmetry.

For example: silicon's conventional cell is a cube, containing 8 atoms, but its primitive cell is that of the face-centered cubic (FCC) lattice, 4 times smaller and containing 2 basis atoms.

(6) Close-packed structures: For further reference here is a comparison of the FCC and HCP close-packed structures:

(a) FCC conventional cell, with the layers colored red-green-blue to show the A-B-C-A-B-C stacking. The structure is the same for each case, but viewed from different angles to show the close-packing layers and how they register.



(b) HCP: Below are similar views of the HCP lattice. In the top two views the A-B-A-B layers are colored alternating blue and green. In the lower figures the corner atoms and center atom of one unit cell have been colored red.

