

PHYSICS 617, 1-18-2017

These notes include an overview of the properties of solids, and their relationships to structures that we will examine later in more detail. Most of the course deals with the study of crystals, containing a periodic array of atoms. This is in part because the study of crystalline materials contributed much to our fundamental understanding of the electronic properties of materials, and the behavior of infinite, ideal periodic crystals still provides the framework for much of our understanding of other condensed matter systems. For comparison, below I have outlined some of the properties of non-crystalline, or polycrystal materials, compared to the ideal crystal case. In addition first we discuss some of the basic categories of electronic behavior, closely related to the electron-gas and electrical transport properties discussed in the beginning chapters of the Ashcroft and Mermin text, and also the way in which electron bands arise in extended crystals.

(1) Classifying solids: Metals vs. Insulators and electrical conductivity.

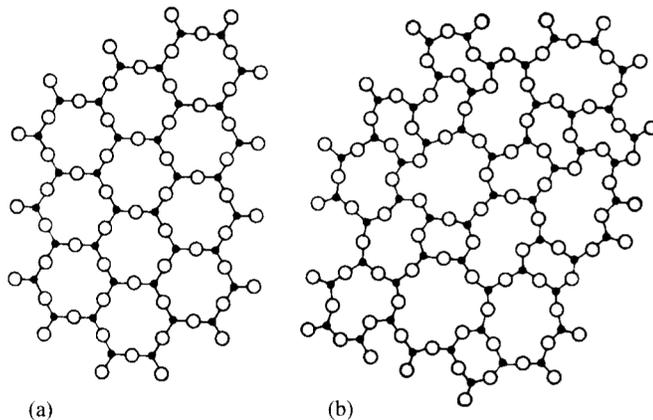
Electrical behavior makes up the first part of this course, and Metal vs. Insulator is one of the essential features distinguishing different materials. The table below shows the four general categories usually defined. Electrical resistivities in different materials cover many orders of magnitude, and the dividing line between neighboring categories is 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 vs T	bandgap (and carrier properties)	bonding
Metal e.g. copper	10^{-5} to 10^{-7} Ω -cm	increases with T	no gap ("electron gas")	Metallic (weak)
Semimetal e.g. bismuth	10^{-3} Ω -cm	increases with T	no gap (small band overlap \sim low-density electron gas)	
Semi-conductor e.g. silicon	10^{-2} to 10^{+9} Ω -cm	decreases with T	small gap (no carriers $T = 0$, carriers introduced thermally or by impurities)	covalent
Insulator e.g. diamond, oxides, molecular solids	10^{14} to 10^{22} Ω -cm	decreases with T	large gap	covalent (strong) to ionic/van der Waals (weak)

(2) Atomic-scale structures

Crystals feature a regular array of atoms. See the schematic figure below contrasting the regular structure of quartz to a glassy structure formed from the same material. Most solid materials prefer to form crystals. For example metals, ice, inorganic materials such as NaCl, and organic molecules will typically form crystals. Even purified samples of macromolecules such as proteins typically have a crystalline arrangement as lowest-energy state; sometimes great effort is placed into growing such crystals as a means toward crystallographic identification of the molecular arrangement.

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.



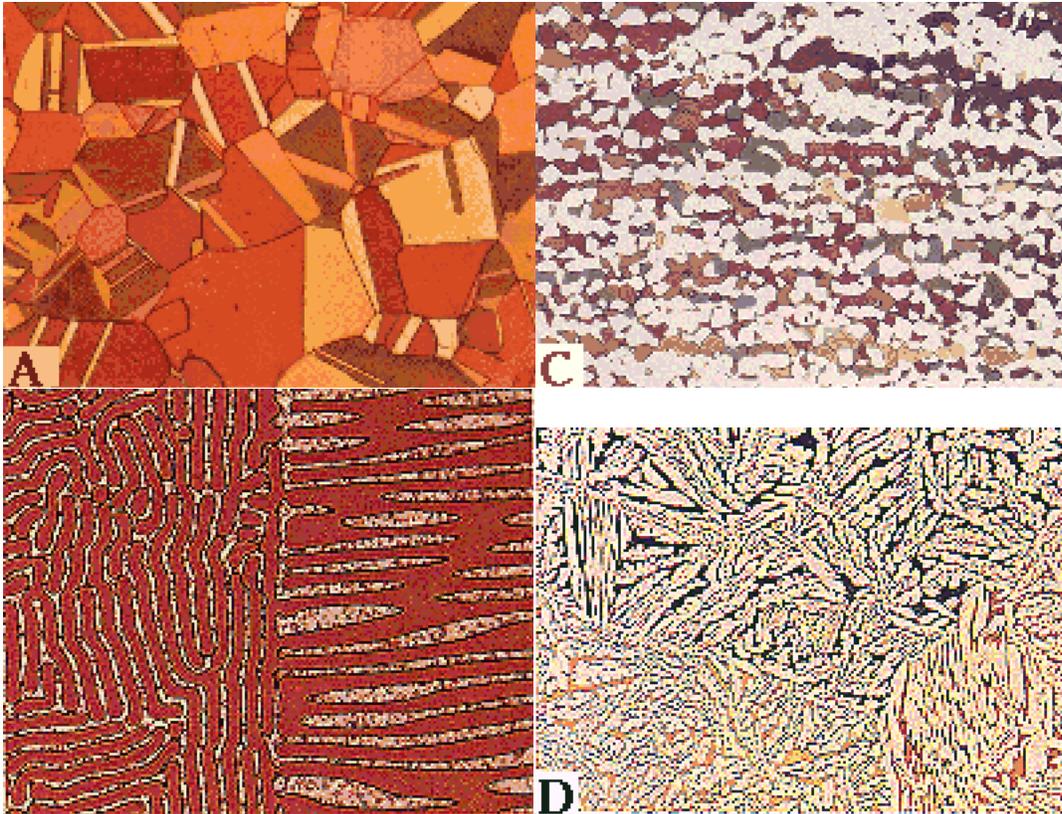
from *Glasses for Photonics*, Yamane and Asahari, Cambridge Univ. Press 2000. For the actual (hexagonal or trigonal) 3d quartz structure see e.g. the crystal database links on the webpage.

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

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 the 2011 chemistry Nobel Prize; such materials have interesting physical properties, and contain two or three-dimensional Penrose tilings. (A two-dimensional Penrose tiling can be seen in the atrium of the MIST institute building.)

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

Large *Single Crystals* occur rarely in nature, but are grown for special purposes, notably Si wafers for electronic circuits, which are cut from 2 m-long essentially perfect crystals. More typically, materials contain a collection of internal crystalline grains arranged in a pseudo-random way. Optical micrographs showing the hidden crystal structure in brass alloys (Cu-Zn) are shown on the next page:



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 included grains of a different phase can be much stronger than a single crystal. This happens because the interfaces and disorder pin dislocations – see chapter 30 in the text. Thus the different materials in the four pictures above will have significantly different strengths, even for grain sizes of 10s of μm (10^{13} atoms). For mechanical properties it is important to know the structure on very large as well as small scales. On the other hand the relevant grain sizes may be very small; in some cases nanostructured materials may become mechanically very strong (approaching “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 occurs on very small length-scales of order 10 nm (10^3 atoms), generally much smaller than the sizes of grains described above. The breakdown of the band-structure concept on these scales is called the electronic size effect. In semiconductor systems, where nm-scale structures can be 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: Electrons in crystals can be approximated as classical particles with a mean free path (see chapters 1, 2, and 13). In perfect specimens at low temperatures, the mean free path may be as much as 100 μm , or even mm sizes. Such behavior can appear in the “two-dimensional electron gas” semiconductor-based devices in which quantum hall effects, and other quantum phenomena, have been seen at low temperatures. However, in more typical materials the mean free path does not exceed 1 μm . This limit represents a size beyond which polycrystals will behave much as if they were infinite-size crystals (for example the micrographs pictured above would be in this category). However, if the grain boundaries themselves scatter strongly, this may significantly reduce the electrical conductivity.

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

Following up on 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:

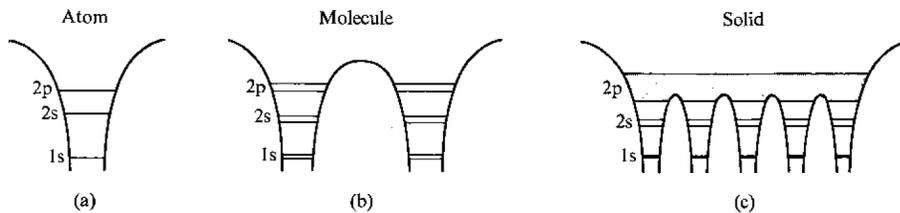


Fig. 5.1 The evolution of the energy spectrum of Li from an atom (a), to a molecule (b), to a solid (c).

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 right-most figure may not show clearly in the scan). Note however that for typical bond lengths these bands don’t maintain pure-*s* or pure-*p* characteristics in the metal. Here is a figure from the book by Mott and Jones providing a more accurate picture (the overlapping bands are mixed):

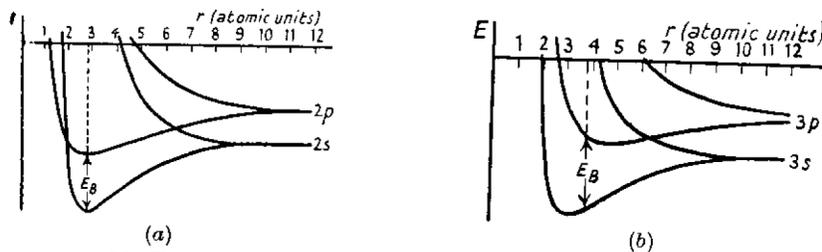
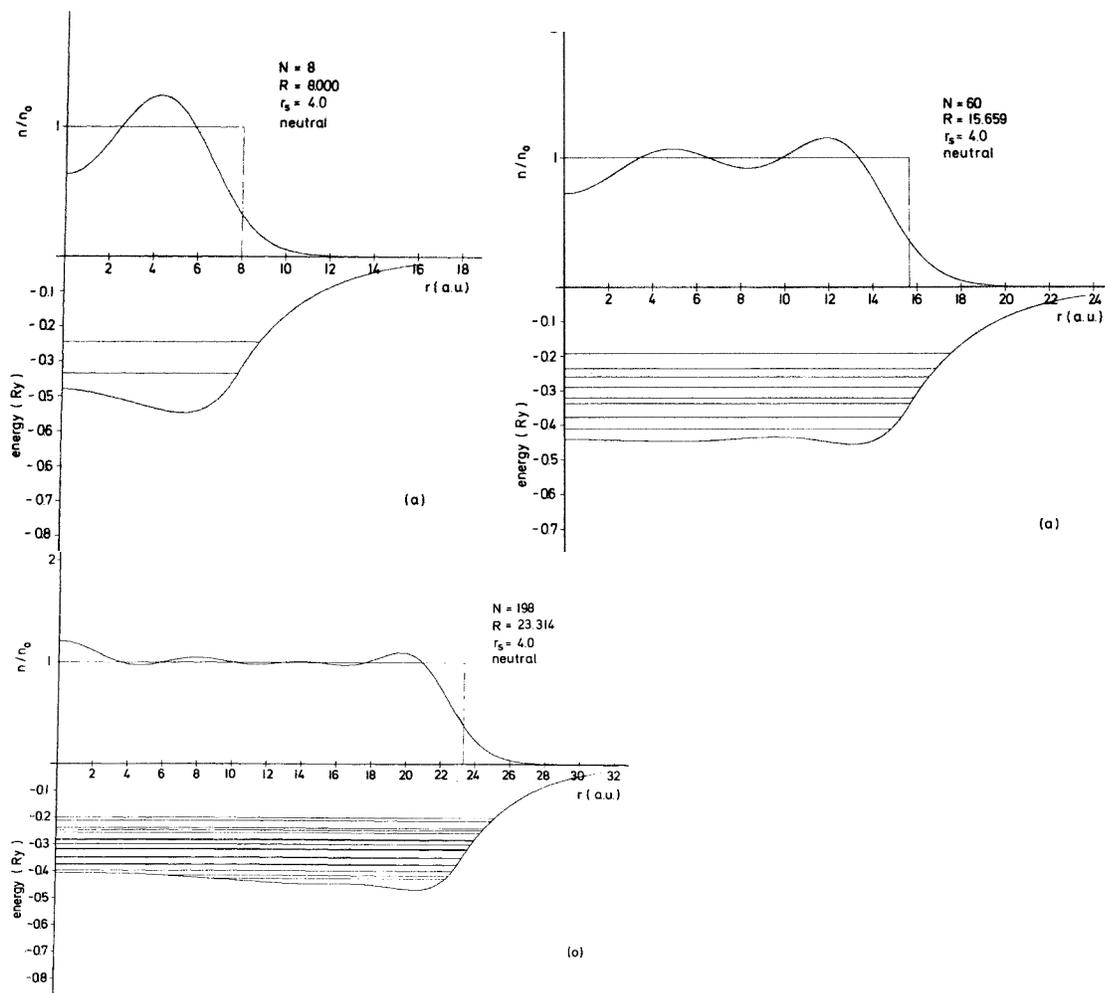


Fig. 36. Energies of states in crystal lattices; (a) lithium, (b) sodium.

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 below are 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.]



We see that even for 198 electrons, the “band” has started to fill in. This cluster contains about the same number of atoms as you would have in a $6 \times 6 \times 6$ -atom crystallite, and its diameter would be about 0.2 nm, with a large fraction of its atoms sitting on the surface. Nevertheless, we can already see the distinctive features of the electron band, which for larger systems acts as a virtual continuum of electronic states. This example illustrates the general feature that one really must go to nano-scale particles before the infinite-crystal approximation runs into serious trouble for ground-state electronic calculations.

Classical Transport Behavior (from Ashcroft & Mermin, ch. 1; this part is a rough outline, rather than detailed notes)

(1) **Electrical conductivity:** The standard relationship is, $\sigma = \frac{ne^2\tau}{m}$, where n = density of electrons (per volume), $1/\tau$ = scattering probability, and m = electron mass.

Beyond the classical Drude picture:

- The relation above can work well in simple cases; more generally correct is to use Boltzmann theory or a more sophisticated statistical theory of scattering (see later chapters & advanced texts), however this relation does provide the basis for many of the conceptual models of transport.

- Even when this relationship is valid, the carriers have either sign, and m should be replaced by m^* , the effective mass. (These are entirely quantum effects.)

- Other useful quantities defined in this section are the mobility $\mu = \frac{e\tau}{m}$, and the radius of the

“electron volume”, $r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$, another measure of the electron density that is often used.

(2) **Hall effect:** Note in this section of A&M, you can replace H/c by B everywhere to get the MKS relationship.

The Hall resistance is, $R_H = -\frac{1}{nec}$. [And its MKS equivalent $R_H = -\frac{1}{ne}$.]

And despite the unrealistic derivation from classical mechanics the results are in many ways generally applicable for real solids: The Hall effect is the standard means to measure carrier density (particularly for semiconductors). Also as noted above, the sign of the carrier charge may be positive or negative, changing the Hall sign to positive for “holes”.

(3) **AC conductivity:** Simple scattering theory yields: $\sigma(\omega) = \frac{\sigma(0)}{1 - i\omega\tau}$.

- This is surprisingly effective in simple cases.

- This result also leads to plasma frequency (see textbook derivation): $\omega_p^2 = \frac{4\pi ne^2}{m}$, and for

example the important concept of “ultraviolet transparency” in metals. Notice that the scattering time drops out of the latter relationship. Plasmon oscillations (described in this section of the text) are another consequence of the AC response; these have in recent years taken on added importance because of the behavior as seen in nano-particles, and for example the relevance to THz electronics and related behavior.

(4) **Thermal conductivity:** A straightforward derivation yields, $\kappa = \frac{1}{3}c\ell v$, with c = heat capacity, ℓ = mean free path, v = rms velocity. In this case the Drude (classical) result is completely wrong (but accidentally very close).

(5) **Thermoelectric effect:** Q is the “Seebeck coefficient”, normally measured in $\mu\text{V/K}$.

- Measured quantities can have either sign; the classical derivation completely fails in this case.

- Can be used in practice to measure m^* , combined with σ and R_H , based on more sophisticated theory (& see ch. 13 in the text).