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Chapter 1 : Introduction to the Electron Theory of Metals - Uichiro Mizutani - Google Books

Metallic solids with an impurity, generally called alloys, are of immense importance from both fundamental and technological points of view. The pioneering work of Bloember gen and Rowland () gave considerable impetus to the study of the electronic structure of metallic alloys.

In metals, heat conductivity is primarily due to free electrons. Following the Wiedemannâ€"Franz law , thermal conductivity of metals is approximately proportional to the absolute temperature in kelvins times electrical conductivity. In pure metals the electrical conductivity decreases with increasing temperature and thus the product of the two, the thermal conductivity, stays approximately constant. However, as temperatures approach absolute zero, the thermal conductivity decreases sharply. Many pure metals have a peak thermal conductivity between 2 K and 10 K. On the other hand, heat conductivity in nonmetals is mainly due to lattice vibrations phonons. Except for high quality crystals at low temperatures, the phonon mean free path is not reduced significantly at higher temperatures. Thus, the thermal conductivity of nonmetals is approximately constant at high temperatures. At low temperatures well below the Debye temperature , thermal conductivity decreases, as does the heat capacity, due to carrier scattering from defects at very low temperatures. An example of this would be the change in thermal conductivity that occurs when ice thermal conductivity of 2. Other examples of materials where the thermal conductivity varies with direction are metals that have undergone heavy cold pressing , laminated materials, cables, the materials used for the Space Shuttle thermal protection system , and fiber-reinforced composite structures. Electrical conductivity[edit] In metals, thermal conductivity approximately tracks electrical conductivity according to the Wiedemannâ€"Franz law , as freely moving valence electrons transfer not only electric current but also heat energy. However, the general correlation between electrical and thermal conductance does not hold for other materials, due to the increased importance of phonon carriers for heat in non-metals. Highly electrically conductive silver is less thermally conductive than diamond , which is an electrical insulator , but due to its orderly array of atoms it is conductive of heat via phonons. Magnetic field[edit] The influence of magnetic fields on thermal conductivity is known as the thermal Hall effect or Righiâ€"Leduc effect. Gaseous phases[edit] Exhaust system components with ceramic coatings having a low thermal conductivity reduce heating of nearby sensitive components Air and other gases are generally good insulators, in the absence of convection. Therefore, many insulating materials function simply by having a large number of gas-filled pockets which obstruct heat conduction pathways. Examples of these include expanded and extruded polystyrene popularly referred to as "styrofoam" and silica aerogel , as well as warm clothes. Light gases, such as hydrogen and helium typically have high thermal conductivity. Dense gases such as xenon and dichlorodifluoromethane have low thermal conductivity. An exception, sulfur hexafluoride , a dense gas, has a relatively high thermal conductivity due to its high heat capacity. Argon and krypton , gases denser than air, are often used in insulated glazing double paned windows to improve their insulation characteristics. The thermal conductivity through bulk materials in porous or granular form is governed by the type of gas in the gaseous phase, and its pressure. At lower pressures, the thermal conductivity of a gaseous phase is reduced, with this behaviour governed by the Knudsen number , defined as K.

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This plasticity stems from the simplicity of the arrangement of atoms in the crystals making up aâ€¦ Classification The definition of a solid appears obvious; a solid is generally thought of as being hard and firm. Upon inspection, however, the definition becomes less straightforward. A cube of butter, for example, is hard after being stored in a refrigerator and is clearly a solid. After remaining on the kitchen counter for a day, the same cube becomes quite soft, and it is unclear if the butter should still be considered a solid. Many crystals behave like butter in that they are hard at low temperatures but soft at higher temperatures. They are called solids at all temperatures below their melting point. A possible definition of a solid is an object that retains its shape if left undisturbed. The pertinent issue is how long the object keeps its shape. A highly viscous fluid retains its shape for an hour but not a year. A solid must keep its shape longer than that. Basic units of solids The basic units of solids are either atoms or atoms that have combined into molecules. The electrons of an atom move in orbits that form a shell structure around the nucleus. The shells are filled in a systematic order, with each shell accommodating only a small number of electrons. Different atoms have different numbers of electrons, which are distributed in a characteristic electronic structure of filled and partially filled shells. The properties of solids are usually predictable from the properties of their constituent atoms and molecules, and the different shell structures of atoms are therefore responsible for the diversity of solids. All occupied shells of the argon Ar atom, for example, are filled, resulting in a spherical atomic shape. In solid argon the atoms are arranged according to the closest packing of these spheres. The iron Fe atom, in contrast, has one electron shell that is only partially filled, giving the atom a net magnetic moment. Thus, crystalline iron is a magnet. The covalent bond between two carbon C atoms is the strongest bond found in nature. This strong bond is responsible for making diamond the hardest solid. Long - and short-range order A solid is crystalline if it has long-range order. Once the positions of an atom and its neighbours are known at one point, the place of each atom is known precisely throughout the crystal. Most liquids lack long-range order, although many have short-range order. Short range is defined as the first- or second-nearest neighbours of an atom. In many liquids the first-neighbour atoms are arranged in the same structure as in the corresponding solid phase. At distances that are many atoms away, however, the positions of the atoms become uncorrelated. These fluids, such as water, have short-range order but lack long-range order. Certain liquids may have short-range order in one direction and long-range order in another direction; these special substances are called liquid crystals. Solid crystals have both short-range order and long-range order. Solids that have short-range order but lack long-range order are called amorphous. Almost any material can be made amorphous by rapid solidification from the melt molten state. This condition is unstable, and the solid will crystallize in time. If the timescale for crystallization is years, then the amorphous state appears stable. Glasses are an example of amorphous solids. In crystalline silicon Si each atom is tetrahedrally bonded to four neighbours. In amorphous silicon a-Si the same short-range order exists, but the bond directions become changed at distances farther away from any atom. Amorphous silicon is a type of glass. Quasicrystals are another type of solid that lack long-range order. Most solid materials found in nature exist in polycrystalline form rather than as a single crystal. They are actually composed of millions of grains small crystals packed together to fill all space. Each individual grain has a different orientation than its neighbours. Although long-range order exists within one grain, at the boundary between grains, the ordering changes direction. A typical piece of iron or copper Cu is polycrystalline. Single crystals of metals are soft and malleable , while polycrystalline metals are harder and stronger and are more useful industrially. Most polycrystalline materials can be made into large single crystals after extended heat treatment. In the past blacksmiths would heat a piece of metal to make it malleable: The smiths would bend the softened metal into shape and then pound it awhile; the pounding would make it polycrystalline again, increasing its strength. Categories of crystals Crystals are classified in general categories, such as insulators, metals, semiconductors, and molecular solids. A single crystal of an insulator is usually transparent and resembles a piece of glass. Metals are shiny unless they have rusted. Semiconductors are sometimes shiny and sometimes transparent but are never rusty. Many crystals can be classified as a single type of solid, while others have intermediate behaviour. Cadmium sulfide CdS can be prepared in pure form and is an excellent insulator; when impurities are added to cadmium sulfide, it becomes an interesting semiconductor. Bismuth Bi appears to be a metal, but the number of electrons available for electrical conduction is similar to that of semiconductors. In fact, bismuth is called a semimetal. Molecular solids are usually crystals formed from molecules or polymers. They can be insulating, semiconducting, or metallic, depending on the type of molecules in the crystal. New molecules are continuously being synthesized, and many are made into crystals. The number of different crystals is enormous. Structure Crystals can be grown under moderate conditions from all 92 naturally occurring elements except helium, and helium can be crystallized at low temperatures by using 25 atmospheres of pressure. Binary crystals are composed of two elements. Crystals can also be formed with three or more elements. The unit cell A basic concept in crystal structures is the unit cell. It is the smallest unit of volume that permits identical cells to be stacked together to fill all space. By repeating the pattern of the unit cell over and over in all directions, the entire crystal lattice can be constructed. A cube is the simplest example of a unit cell. Two other examples are shown in Figure 1. The first is the unit cell for a face-centred cubic lattice, and the second is for a body-centred cubic lattice. These structures are explained in the following paragraphs. There are only a few different unit-cell shapes, so many different crystals share a single unit-cell type. An important characteristic of a unit cell is the number of atoms it contains. The total number of atoms in the entire crystal is the number in each cell multiplied by the number of unit cells. Copper and aluminum Al each have one atom per unit cell, while zinc Zn and sodium chloride have two. Most crystals have only a few atoms per unit cell, but there are some exceptions. Crystals of polymers, for example, have thousands of atoms in each unit cell. Created and produced by QA International. The most common lattice structures for metals are those obtained by stacking the atomic spheres into the most compact arrangement. There are two such possible periodic arrangements. In each, the first layer has the atoms packed into a plane-triangular lattice in which every atom has six immediate neighbours. Figure 2 shows this arrangement for the atoms labeled A. The second layer is shaded in the figure. It has the same plane-triangular structure; the atoms sit in the holes formed by the first layer. The first layer has two equivalent sets of holes, but the atoms of the second layer can occupy only one set. The third layer, labeled C, has the same structure, but there are two choices for selecting the holes that the atoms will occupy. Cadmium and zinc crystallize with this structure. The second possibility is to place the atoms of the third layer over those of neither of the first two but instead over the set of holes in the first layer that remains unoccupied. Copper, silver Ag , and gold Au crystallize in fcc lattices. In the hcp and the fcc structures the spheres fill 74 percent of the volume, which represents the closest possible packing of spheres. Each atom has 12 neighbours. The number of atoms in a unit cell is two for hcp structures and one for fcc. There are 32 metals that have the hcp lattice and 26 with the fcc. Another possible arrangement is the body-centred cubic bcc lattice , in which each atom has eight neighbours arranged at the corners of a cube. Figure 3A shows the cesium chloride CsCl structure, which is a cubic arrangement. If all atoms in this structure are of the same species, it is a bcc lattice. The spheres occupy 68 percent of the volume. There are 23 metals with the bcc arrangement. Stacking of spheres in closest-packed arrangements. There is an equal number of the two types of ions in the unit cell of the A cesium chloride, B sodium chloride, and D zinc blende arrangements.

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