The metallic bond

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1   Introduction

Metals are defined by their ability to conduct electricity at absolute zero[1]. The distinction between a metal and an insulator can be made only at absolute zero. The electrical conductivity of an insulator increases with temperature, although in common insulators the increase may be very small indeed. In this essay I will argue that whether or not a material conducts electricity at absolute zero is largely irrelevant to its chemical bonding.

The metallic bond is a type of covalent bond because it originates from the sharing of electrons. Bonds in a covalent insulator like diamond are saturated. The bond between each pair of carbon atoms in diamond comprises two shared electrons, one from each atom. In a metal there are not enough electrons to form saturated bonds to all the neighbours of an atom. The bonds are unsaturated because they comprise less than two electrons per pair of atoms.

There are two principal classes of metallic bonding[2]: (i) the 'simple metals' dominated by sp-bonding, and (ii) the transition metals dominated by dd-bonding. I will show that cohesion in both classes is attributable to unsaturated covalent bonds.

The elements of groups 1, 2 and 3 and tin and lead in group 4 are often called 'simple metals'. Nearly all their cohesion is provided by a purely density-dependent energy. Differences in the energies of alternative crystal structures with the same density are much smaller, typically of order $1 - 10$ kJ/mole[3].

In the transition metal series the filling of the d-shell dominates cohesion, and it determines the systematic changes in crystal structure as we move across the 4d and 5d series. The same is true of the 3d series but the occurrence of magnetism is a complication.

The following misleading statements about metals are often encountered in elementary text-books and in well-meaning tutorials and videos on the internet:

1st misleading statement: In an insulator the outer shell electrons are *localised*, either on individual atoms forming ionic bonds as in sodium chloride, or between pairs of atoms in covalent bonds as in diamond. This localisation of the outer shell electrons in an insulator renders them unable to conduct electricity. In contrast, the outer shell electrons of a metal are *delocalised*, so that they are free to conduct electricity.

Comment: Localisation of electrons means they are confined to a small region within the material, either on an atom in an ionic material or in a bond in a covalent material. For example, inner shell electrons (also called core electrons) are localised to a small region around the nucleus because they are unable to escape its strong attraction.

Electrons in an incomplete outer shell of an atom are called valence electrons. When atoms of a metal are brought together to create the metallic state the valence electrons are liberated and move throughout the entire metal, forming a 'gas' (or 'sea') of delocalised electrons. The freedom of these electrons enables them to conduct electricity. They are called conduction electrons to distinguish them from core electrons which are unable to escape the nuclei to which they are bound. The valence electrons of the atoms become the conduction electrons of the metal.

It is misleading to say that all insulators are not electronic conductors because electrons in the outer shells are localised. For example, diamond is an excellent insulator. But its valence electrons are in *molecular* orbitals in which they hop from atom to atom throughout the entire crystal: they are no less itinerant than conduction electrons in aluminium. Paradoxically this picture is completely

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[1] This definition originates from Sir Nevill Mott: see P P Edwards et al., Phil. Trans. R. Soc., A **368**, 941 (2010).

[2] Bonding in the f-block metals (i.e. the lanthanides and the actinides) has similarities to bonding in the transition metals. The main difference is that electrons in f-states have an even smaller spatial extent than those in d-states. This leads to stronger electron repulsion between electrons in f-states, which plays a central role in the chemistry and physics of f-block metals. Bonding in f-block metals is an area of current research.

[3] Chemists tend to use kilojoules per mole (kJ/mole) of some particle. Physicists tend to use electron volts per particle (eV/particle). To convert quickly between them 100 kJ/mole is roughly 1 eV/particle.

consistent with the chemist's picture of localised electrons in saturated covalent bonds in diamond[4]. As we shall see in section 5 diamond is an insulator for reasons that have nothing to do with localisation of electrons. The same applies to an alkane molecule. The valence electrons in an alkane are in molecular orbitals, where they hop freely from atom to atom throughout the molecule, even though all bonds are saturated and covalent. Alkanes are good electrical insulators even though the valence electrons are delocalised.

When it exists, localisation of the valence electrons in a solid does result in an electronic insulator. But there are many covalent (and ionic) insulators in which valence electrons are delocalised. The reasons why some materials are electronic conductors at absolute zero and others are not will be discussed in section 5.

2nd misleading statement: The ion cores of the metal are surrounded by the free electron gas. Since the ion cores are positively charged and the conduction electrons are negatively charged they attract each other. Their attraction binds the metal together.

Comment: Equivalent statements appear in some A-level syllabuses in chemistry and the International Baccalaureate qualification in chemistry. The statement is misleading because the electrostatic attraction between the ion cores and the electron gas is insufficient by itself to bind the atoms of the metal together.

The statement is a very one-sided account of the energy balance associated with the creation of the electron gas in a metal. The liberation of the outer electrons amounts to ionizing the atoms, which requires a considerable amount of energy. For example, in aluminium each atom contributes three conduction electrons leaving behind an Al^{3+} ion. The first three ionisation energies of aluminium amount to 5,140 kJ/mole (53 eV per atom). That is more than ten times the cohesive energy of aluminium. In addition, the liberated electrons enter an electron gas where they repel each other electrostatically. The positive energy of their repulsion has also been overlooked in the second statement. For the metal to be stable against separating into its constituent atoms these large positive energies have to be offset by an even larger negative energy. It is not obvious that the negative energy of the electrostatic attraction between the ion cores of the metal and the liberated conduction electrons is sufficient. As we shall see in section 3, this attractive interaction is considerably weaker than might be expected from electrostatics alone. It turns out it is not enough to bind the atoms of the metal together.

3rd misleading statement: Resistance in metallic conductors is caused by collisions between electrons and positive ions of the crystal lattice.

Comment: When an electric current flows in a metal the metal heats up. This happens because current-carrying electrons transfer some of their energy to ions in the crystal. The resistance of a metal is all about the processes that result in this transfer of energy.

When there is a current flowing these energy transfers occur at imperfections in the crystal, such as impurities, and structural defects, such as missing atoms. They also occur when current-carrying electrons interact with vibrations of the atomic structure of the crystal. As a result the resistance of a metal increases with increasing temperature[5], which is a characteristic property of metals. In contrast, the resistance of an insulator decreases with increasing temperature for reasons that will be explained in section 5. The third statement is misleading because it omits the essential point that electrical resistance of metals is due entirely to deviations from the periodic structure of the perfect

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[4]Consider the bond in a hydrogen molecule. It is often depicted with the two electrons localised between the atoms forming a saturated covalent bond. In a more sophisticated description the electrons are in a bonding molecular orbital where they are constantly hopping back and forth between the atoms. In this picture they are delocalised over both atoms and there is an accumulation of electronic charge between the atoms. The first description is just a caricature of the second.

[5]An aside: provided the metal does not become a superconductor, quantum physics shows the resistance remains finite even at absolute zero due to spontaneous emission of quantised atomic vibrations (phonons).

crystal caused by atomic vibrations and crystal defects.

4th misleading statement: The delocalised nature of bonding in metals enables planes of atoms to slide over each other relatively easily compared to insulators. Sketches in books and movies on the internet show whole planes sliding *en masse* over each other. This is why metals are malleable and ductile whereas insulators are brittle. Metals are strengthened when impurities are added because the planes become distorted by the impurities and then it becomes more difficult for the planes to slide over each other.

Comment: There is a lot here to unpick.

In crystalline materials plastic deformation[6] does take place by atomic planes sliding over each other. However, it most emphatically does not occur by entire planes of atoms sliding *en masse* over each other. Instead sliding begins in small patches of a plane and the patches subsequently expand (see Fig.1). The boundary of a patch is a linear defect called a *dislocation*. Plastic deformation in all crystalline materials centres on the formation and movement of dislocations[7]. The strength and degree of directional bonding does affect the mobility of dislocations. But there are other factors, at least as important, such as the ambient temperature, alloying, and the history of thermal and mechanical treatments to which the material has been subjected. In general, the interaction between dislocations and impurity atoms reduces the mobility of dislocations and increases the strength of a metal. There are movies on the internet of dislocations moving in crystals, as seen in a transmission electron microscope, e.g. see https://www.youtube.com/watch?v=BV1cxwxnhPs&ab_channel=OndrejKotecky. An excellent model of defects in crystals is the bubble raft, although it is only two-dimensional, e.g. see Sir Lawrence Bragg's beautiful video of a bubble raft at https://www.youtube.com/watch?v=UEB39-jlmdw.

Secondly, some pure metals are not malleable at low temperatures. For example, pure iron, tungsten and molybdenum are brittle at low temperatures. As the temperature is raised they pass through a 'brittle to ductile transition', whereupon they become ductile, but the bonding between atoms barely changes. This experimental fact is a clear indication that the ductility of these metals and alloys is only indirectly related to bonding in them. But it is directly related to the mobility of dislocations in these metals, which increases very rapidly with temperature at the brittle to ductile transition. Some ordered intermetallic alloys[8] remain very brittle up to their melting points. If any of these metals and alloys are hit sufficiently hard with a hammer while they are in a brittle state they break rather than deform, just like glass or porcelain.

Thirdly some insulating crystals also display a brittle to ductile transition. For example, at room temperature silicon and diamond are brittle, but they become more ductile if the temperature is raised sufficiently.

Fourth, in steels minute concentrations (parts per million) of antimony, tin, sulphur and phosphorus can lead to severe embrittlement without affecting bonding throughout the overwhelming majority of the material. Minute quantities of hydrogen embrittle many metals and alloys.

The relationship between the mechanical properties of materials and their chemical bonding is far more complex than the fourth misleading statement suggests.

Having become aware of the prevalence of these misleading statements I decided to write this essay about bonding and selected properties of metals and alloys for teachers of chemistry and physics. I have avoided the quantum mechanics and mathematical derivations involved in a deeper understanding of metallic bonding. There is a list of books in the bibliography for the interested reader to delve further into the subject. My goal here is to provide an accessible picture of bonding in metals.

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[6]Plastic deformation occurs when an applied load changes the shape of a sample permanently. It differs from elastic deformation which is fully reversed when the load is removed.

[7]Some crystals deform plastically through the nucleation and growth of three-dimensional sheared regions called 'deformation twins'. However, even these defects involve the creation and movement of stacks of dislocation loops.

[8]An ordered intermetallic alloy is a stoichiometric metallic compound such as Al_3Ti, FeAl, TiAl and $MoSi_2$.
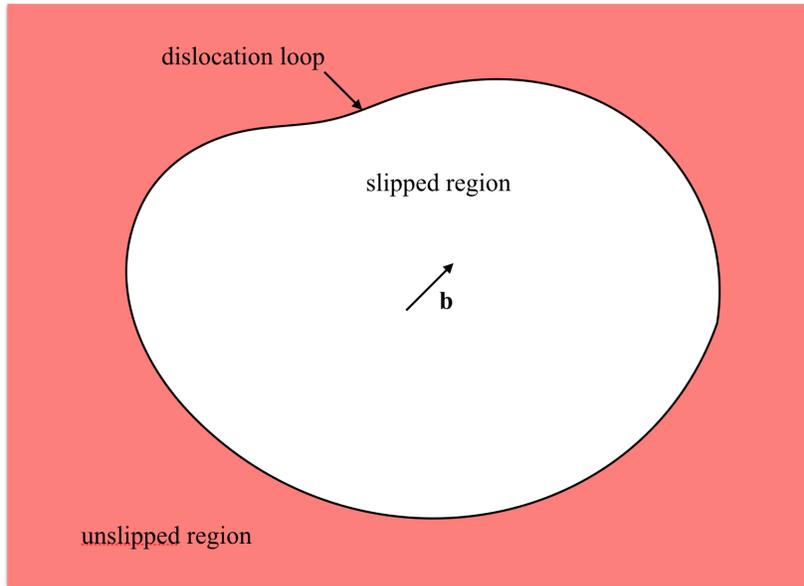
Figure 1: A dislocation loop lying in a slip plane separating slipped and unslipped regions. The dislocation is the line separating the slipped and unslipped regions of the slip plane. It forms a loop. Inside the loop the material beneath the slip plane has slipped with respect to material above it by the vector **b**, which is known as the Burgers vector.

2 Jellium

The simplest model of a metal is jellium. Consider a mole of a metal with molar volume V_m. The number of valence electrons of a metal atom is called the valency of the metal and we label it z. The total number of conduction electrons is $N_A z$ per mole, where N_A is Avogadro's number (6.022×10^{23}). The average density of conduction electronic charge is $\rho = -N_A z e / V_m$, where $-e$ is the charge of an electron. It is an average because the presence of the ions introduces local variations in the local electronic charge density. The charge of each metal ion is $+ze$. The metal is turned into jellium by smearing out the ions into a uniform positive background charge with density $+N_A z e / V_m$. This process also eliminates local variations in the conduction electron density, which is now $\rho = -N_A z e / V_m$ everywhere, except, as we shall see, at the surface of the metal. Within a fraction of a nanometre from the surface of jellium every point within it is electrically neutral. Jellium is so called because the absence of atomic structure resembles a metallic jelly.

Consider an electron in the vacuum at a distance d from the jellium surface. The electric field of the vacuum electron repels some of the conduction electrons in the jellium surface, exposing some of the positive background charge density. Consequently the vacuum electron is attracted to the jellium surface. At the jellium surface the strength of the electric field of the vacuum electron increases as d decreases, and the change in the surface charge density becomes larger and more concentrated in the region closest to the vacuum electron. When the vacuum electron enters the jellium it continues to repel conduction electrons near it. In other words there is a local depletion in the conduction electron density surrounding the vacuum electron. The local depletion exposes some of the positive background charge density. There is an attractive electrostatic interaction between the vacuum electron and the exposed positive charge. The local depletion of the conduction electron density is called a 'correlation hole'. It arises because electrons repel each other electrostatically. Once the vacuum electron enters the metal it becomes indistinguishable from conduction electrons. Each conduction electron has its own correlation hole from which it can be separated only when it leaves the metal. The lowering of the energy of each conduction electron through the interaction with its correlation hole is called the

correlation energy[9].

Let the number of conduction electrons per cubic metre in jellium be n. Then $n = N_A z / V_m$. The dependence of the correlation energy of jellium on n has been computed using quantum mechanics. It is given quite accurately by the following formula[10]:

$$
\begin{aligned}
E_c &= -93.98\, z\, \log_{10}\left(1 + 1.745 \times 10^{-9} n^{1/3} + 1.489 \times 10^{-19} n^{2/3}\right) \ \text{kJ/mole} \\
&= -0.9740\, \log_{10}\left(1 + 1.745 \times 10^{-9} n^{1/3} + 1.489 \times 10^{-19} n^{2/3}\right) \ \text{eV per electron.}
\end{aligned}
\tag{1}
$$

Throughout this essay the mole refers to N_A metal atoms, each contributing z electrons.

In quantum mechanics there is another source of interaction between electrons. It arises from the Pauli exclusion principle and it is called the *exchange energy*. It creates an effective additional repulsion between electrons of the same spin. The correlation hole is enlarged by this interaction because other electrons with the same spin as the electron in the hole are repelled. The hole created by the combined effects of electron correlation and exchange is called the exchange-correlation hole. It contains one missing electron, equivalent to one smeared out proton of the positive background charge density. In jellium it is a spherical hole, except at the surface of jellium where its shape is distorted. When it is spherical it is like an inside-out hydrogen atom, with an electron at the centre and a positive charge density distributed around it. The combination of an electron and its exchange-correlation hole is called a quasiparticle to emphasise they are inseparable within the metal. The quasiparticle has a radius of about 0.1nm, which is very much larger than an isolated electron. Since quasiparticles are electrically neutral they interact with each other electrostatically much more weakly than bare electrons stripped of their neutralising exchange-correlation holes. This is the basis of the free electron approximation where interactions between electrons in a metal are ignored and they move independently of each other. It is somewhat paradoxical that the approximation works only because the interactions between electrons are in fact very strong.

The exchange energy, E_x, is negative because electrons of the same spin are forced further apart, which reduces the positive energy of repulsion between them. It depends on the electron density as follows[11]:

$$
\begin{aligned}
E_x &= -1.0261 \times 10^{-7}\, z\, n^{1/3} \ \text{kJ/mole,} \\
&= -1.0635 \times 10^{-9}\, n^{1/3} \ \text{eV per electron.}
\end{aligned}
\tag{2}
$$

The energy of interaction between each electron and its exchange-correlation hole is called the *exchange-correlation energy*, E_{xc}. It is negative, and it is equal to the sum of E_c and E_x in eqs 1 and 2.

Finally consider the *kinetic energy*, E_k, of the conduction electrons. Electrons obey the laws of quantum mechanics and their kinetic energy[12] can be found only by using those laws. E_k is positive and it varies with the electron density as follows:

$$
\begin{aligned}
E_k &= 2.1110 \times 10^{-17}\, z\, n^{2/3} \ \text{kJ/mole} \\
&= 2.1878 \times 10^{-19} n^{2/3} \ \text{eV per electron.}
\end{aligned}
\tag{3}
$$

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[9]The correlation energy includes a correction to the kinetic energy of the conduction electrons (as computed in eq 3) which is also modified when electron-electron interactions are taken into account.

[10]Teepanis Chachiyo, J. Chem. Phys. **145**, 021101 (2016).

[11]R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, The International Series of Monographs on Chemistry, Oxford University Press: Oxford (1989), p. 108.

[12]The kinetic energy in eq 3 is for non-interacting electrons. The correction arising from electron-electron interactions is included in eq 1, as mentioned in footnote 9.
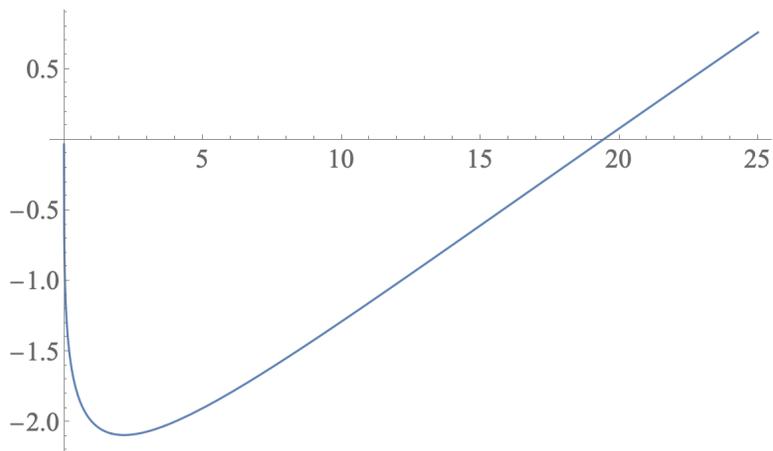
Figure 2: The total energy of jellium in eV per electron along the vertical axis plotted against the conduction electron density in multiples of 10^{28} electrons per cubic metre.

Ignoring its surface, the total energy of jellium E_T is the sum of eqs 1, 2 and 3, and it is plotted in Fig.2. The horizontal axis spans the range of conduction electron densities found in most metals. For example, sodium has z=1 and $n = 2.5 \times 10^{28}$ m^{-3}, magnesium has z=2 and $n = 8.6 \times 10^{28}$ m^{-3}, and aluminium has z=3 and $n = 18.1 \times 10^{28}$ m^{-3}. Two features of this plot stand out. The first is the minimum at an electron density of 2.1×10^{28} m^{-3} where the total energy is -2.1 eV per electron. This is only slightly less than the electron density of sodium, although the binding energy of sodium is only -1.1 eV per electron. Secondly at electron densities beyond about 19.5×10^{28} m^{-3} the total energy is positive. What do we make of these results?

The binding energy of a solid is the reduction in energy when atoms are brought from infinite separations to their final positions of equilibrium in the solid at absolute zero. It is the negative of the cohesive energy (which is also the atomisation energy at absolute zero), which is the energy associated with the reverse process. Since atoms in jellium have been smeared out the total energy plotted in Fig.2 cannot be interpreted as a binding energy. Nevertheless, Fig.2 shows we can expect the exchange-correlation energy to make a significant contribution to the binding energy in an atomistic model of a metal. This expectation is borne out in the section 3.

At the surface of jellium conduction electrons spill over the edge of the positive background charge density into the vacuum. The extent of the spillover has been calculated for different conduction electron densities[13]. These calculations enable the dependence of the energy per unit area of the jellium surface to be estimated. Lang and Kohn found the surface energy of jellium is negative when the electron density exceeds 12×10^{28} m^{-3}. This is less than the conduction electron density of aluminium! At these higher electron densities jellium can reduce its energy by spontaneously breaking into ever smaller pieces, exposing more surface area. We know this does not happen in aluminium or other metals.

In the next section we consider a more realistic model of a metal by retaining its discrete atomic structure.

3 Simple metals

The valence electrons of simple metals are in s and p states only. Examples include sodium in group 1, magnesium in group 2 and aluminium in group 3. As a first approximation, bonding in these

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[13]N.D. Lang and W. Kohn, Phys. Rev. B **1**, 4555 (1970)

metals may be described by a model in which positive metal ions are immersed in a gas of conduction electrons. We shall now consider various contributions to the binding energy.

To liberate the z valence electrons of each atom we must supply the sum of the first z ionisation energies. Let this sum be E_i. The liberated electrons are the conduction electrons of the metal. The binding energy E_B of the metal is the sum of (i) the ioniziation energy E_i, (ii) the energy of the electron gas and (iii) the energy of the ion cores immersed in the electron gas. E_B has to be negative for the metal to be stable against disintegrating into its constituent atoms.

It turns out conduction electrons interact with ion cores much more weakly than expected. Why? This is a quantum effect and it arises from the Pauli exclusion principle - the same principle that gave rise to the exchange energy. The exclusion principle prohibits a conduction electron from entering a fully occupied core state[14]. Therefore, in an ion core a conduction electron experiences an effective repulsion, which counteracts the electrostatic attraction. The cancellation is almost complete. To a reasonable approximation the effective potential acting on a conduction electron inside the ion core is zero. This is called the Ashcroft empty core potential.

There are no electrons in p-states in the cores of lithium and beryllium. Consequently the exclusion principle does not prohibit conduction electrons from having some 2p-character in the cores of these atoms. The repulsion of conduction electrons due to the exclusion principle in these cores is less effective. Conduction electrons experience a stronger interaction with the ion cores of lithium and beryllium than other elements in groups 1 and 2. For this reason lithium and beryllium are not typical simple metals.

A crystalline simple metal may be modelled by a lattice of empty core potentials immersed in a free electron gas. Since the empty core potentials perturb the free electron gas only weakly we assume the electron gas remains uniformly distributed. In this approximation we are ignoring the zero point energy of the metal, which is the energy of quantum atomic vibrations at absolute zero. More importantly, we are also ignoring terms in the energy that depend on the crystal structure. The contributions to E_B we shall include depend only on the *density* of the electron gas. Each atom of the metal may be modelled as an electrically neutral sphere containing an ion core in the middle and z uniformly distributed conduction electrons, as sketched in Fig.3. Since each of these atomic spheres is electrically neutral we neglect the electrostatic interaction energy between different atomic spheres. We also ignore the overlap between atomic spheres.

Consider the potential at a distance r from the centre of an ion core as felt by a conduction electron. Let R_s be the radius of the atomic sphere and let R_c be the radius of the ion core. The potential is zero for $0 < r < R_c$ and $+ze/(4\pi\varepsilon_0 r)$ for $R_c < r < R_s$, where ε_0 is the permittivity of free space and is equal to 8.8542×10^{-12} in SI units. The potential is sketched in Fig. 4. The electrostatic energy E_{es} within each sphere is the sum of (i) the positive (repulsive) interaction energy between the conduction electrons and (ii) the negative (attractive) interaction energy between the conduction electrons and the empty core potential.

The electrostatic energy E_{es} in SI units is as follows:

$$
\begin{aligned}
E_{es} &= \frac{3ze^2}{20\pi\varepsilon_0 R_s} - \frac{3ze^2}{8\pi\varepsilon_0 R_s}\left(1 - \left(\frac{R_c}{R_s}\right)^2\right) \text{ per electron,} \\
&= 8.3361 \times 10^{-8}\frac{z^2}{R_s} - 2.0840 \times 10^{-7}\frac{z^2}{R_s}\left(1 - \left(\frac{R_c}{R_s}\right)^2\right) \text{ kJ/mole.} \quad (4)
\end{aligned}
$$

The first term on the right is the electrostatic interaction energy between conduction electrons within the atomic sphere. The second term on the right is the interaction energy between conduction electrons in the atomic sphere and the empty core potential. Note that in these formulae R_c and R_s are expressed in metres.

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[14]In the language of quantum mechanics the wave function of the conduction electron has to be orthogonal to the wave functions of the occupied core states.
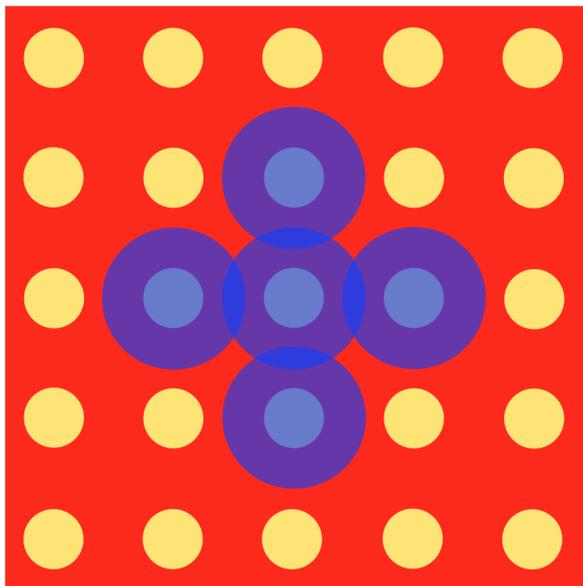
Figure 3: To illustrate a simple metal with ion cores in yellow embedded in a uniform electron gas shown in red. The atomic spheres are shown in blue. The charge on the electrons in each atomic sphere neutralises the charge of the ion core in the middle of the atomic sphere. Notice the small overlap between atomic spheres, which is neglected in the calculation of the electrostatic energy of the system.

The binding energy, E_B, of the metal is the sum of E_i, E_c, E_x, E_k and E_{es}. The latter four energies are evaluated in eqs 1, 2, 3 and 4. Table 1 lists the terms for sodium, magnesium and aluminium and compares the estimated and experimental values of the binding energy. It is seen that the theoretical binding energies have the correct order of magnitude and they show the same trend with increasing z as the experimental values. In this model the theoretical binding energy is the difference between two much larger energies, namely E_i and $E_c + E_x + E_k + E_{es}$. In view of all the approximations involved in the model it is quite remarkable that the predicted binding energies agree with the experimental values as well as they do.

The model shows that in simple metals the conduction electrons do act as a glue between the ion cores. But the glue is not only the electrostatic attraction between the ion cores and the conduction electrons. Electron-electron interactions, which are responsible for the exchange-correlation energy $E_x + E_c$, make an essential contribution to the binding energy, reducing the electrostatic repulsion in the electron gas. If $E_x + E_c$ were ignored the metals would not be bound because E_B would be large and positive.

3.1 Embedded atom model

The picture of an sp-bonded metal as ion cores immersed in an electron gas suggests that bonding in these metals does not have the same restrictions as electron-pair bonding between nearest neighbours in covalent insulators. In the close-packed structures adopted by metals and alloys there are too many neighbours to form saturated bonds, each containing two electrons. Instead we may think of each atom in a metal as being embedded in the tails of the electronic charge densities provided by its neighbours. This is the embedded atom model of bonding in metals.

There are two contributions to the energy of an atom in this model. The first contribution is a sum of pairwise repulsive interactions between the atom and each of its neighbours. As two atoms
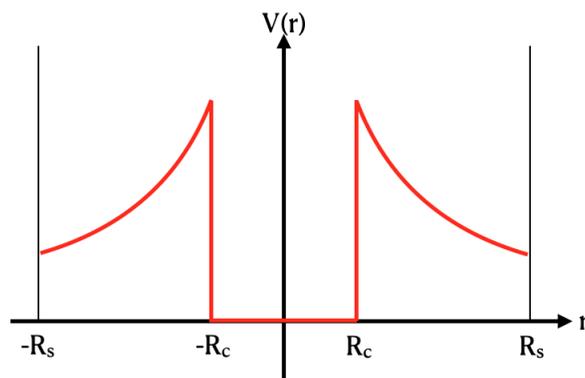
Figure 4: To illustrate the Ashcroft empty core potential $V(r)$. Inside the core radius R_c the potential is zero. Between the core radius and the atomic sphere radius R_s the potential is $+ze/(4\pi\varepsilon_0 r)$.

Metal	n	R_s	R_c	E_i	E_c	E_x	E_k	E_{es}	E_B	$E_B(\text{expt})$
Na	2.53	2.11	0.93	496	-82	-301	182	-402	-107	-110
Mg	8.61	1.77	0.69	2188	-200	-906	823	-2104	-199	-152
Al	18.09	1.58	0.59	5140	-337	-1741	2026	-5470	-382	-327

Table 1: Comparison of theoretical and experimental values of the binding energy (E_B) of the simple metals sodium, magnesium and aluminium. The electron density n is expressed as a multiple of 10^{28} per cubic metre; it is calculated using experimental values of the crystal lattice parameters. R_s and R_c are expressed as multiples of 10^{-10} metres. E_i, E_c, E_x, E_k, E_{es}, E_B and $E_B(\text{expt})$ are expressed in kJ/mole. $E_B = E_i + E_c + E_x + E_k + E_{es}$ is the theoretical estimate of the binding energy. $E_B(\text{expt})$ is the experimental value of the binding energy. R_s and R_c are from L A Girifalco, Acta Metall., **24**, 759 (1976). The ionisation energies E_i and experimental values of the binding energy $E_B(\text{expt})$ are from N N Greenwood and A Earnshaw *Chemistry of the elements*, Pergamon Press: Oxford (1990).

come closer together their electron clouds start to overlap. The exclusion principle counteracts the increase in the electron density between the nuclei. This redistribution of the electron clouds due to the exclusion principle exposes the ion cores more to their electrostatic repulsion. The second contribution to the energy of an atom is an attractive, many-body interaction. It is described as many-body because it depends on the positions of all the neighbours collectively, since they all contribute to the electronic charge density in which the atom is embedded.

One of the most interesting features of the many-body interaction is that when the number of neighbours of an atom in a metal is decreased the strength of the remaining bonds is increased. This is a characteristic feature of metallic bonding. Atoms at the surface of a metal suffer such a reduction in the number of their neighbours. Consequently bonds between atoms in the surface layer are stronger than they are in the bulk. If atoms in the surface layer were not constrained to have the same bond length as atoms in the bulk they would adopt a smaller bond length due to the increased strength of the bonds between them. But in general they are constrained to keep the same bond length as in the bulk. The result is that the surface layer of atoms of most metals is in a state of tension. This is the origin of the tensile surface stress of most solid metals. The bonds between atoms in the surface layer and layers beneath are also stronger. This decreases the spacing between the surface layer and layers beneath, as observed experimentally using diffraction techniques.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	
3d	HCP	HCP	BCC	BCC	BCC	BCC	HCP	FCC	FCC	← cohesive energy kJ/mole
	376	468	512	395	282	413	424	428	336	← melting point ºC
	1541	1673	1929	1860	1247	1538	1497	1455	1085	← bulk modulus GPa
	44	105	162	190	60	168	191	186	137	
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	
4d	HCP	HCP	BCC	BCC	HCP	HCP	FCC	FCC	FCC	← cohesive energy kJ/mole
	422	603	730	658	661	650	554	376	284	← melting point ºC
	1528	1855	2477	2622	2204	2254	1963	1554	962	← bulk modulus GPa
	37	83	170	273	(297)	321	270	181	101	
	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	
5d	HCP	HCP	BCC	BCC	HCP	HCP	FCC	FCC	FCC	← cohesive energy kJ/mole
	428	621	782	859	775	788	670	564	368	← melting point ºC
	1665	2231	3020	3422	3186	3033	2447	1772	1065	← bulk modulus GPa
	41	109	200	323	372	(418)	355	278	173	

Figure 5: The 3d, 4d and 5d transition metal series showing, for each element, the crystal structure (HCP = hexagonal close packed, FCC = face centred cubic and BCC = body centred cubic), the cohesive energy in kJ/mole, the melting point in $^{\circ}$C and the bulk modulus in GPa. 1 GPa is 10^{9} Pa, and 1 Pa is 1 Pascal, which is 1 Newton per square metre. Values in brackets are estimates. Source: Charles Kittel, *Introduction to Solid State Physics*, 6th edn., John Wiley & Sons: New York (1986).

4 Transition metals

The transition metals are not described well by the free electron model of section 3. The d-electrons in the outer shells of transition metals are closer to the nucleus than the outermost s-electrons. This reduces the overlap between d-orbitals on neighbouring atoms, compared with outer shell s-orbitals. Electrons in transition metals occupy giant molecular orbitals formed as linear combinations of the outermost s- and d-orbitals on all the atoms in the metal. In a transition metal all electrons in the outer shells of atoms are itinerant, hopping from atom to atom throughout the metal. This is very similar to the valence electrons in diamond, which occupy molecular orbitals formed from linear combinations of 2s and 2p atomic states, and which are also itinerant. Atomic d-states in the transition metals form directional, unsaturated covalent bonds with their neighbours producing some of the largest cohesive energies of all the elements.

Fig.5 shows the crystal structures, cohesive energies, melting points and bulk moduli of the 3d, 4d and 5d transition metals series. The bulk modulus determines the resistance of the metal to compression; the larger the bulk modulus the more difficult it is to compress the metal. The BCC, FCC and HCP crystal structures are shown in Fig.6. As we cross the 4d and 5d series we see the cohesive energy, melting point and bulk modulus rise to a maximum in the middle of the series and then fall. These trends are less apparent in the 3d series owing to the occurrence of magnetism in Fe, Co and Ni.

The explanation for these trends is as follows. As we cross the series the d-states are being filled by electrons, from 1 on the left to 10 on the right. As the number of electrons increases from 1 to 5 they go into bonding d-states. In the middle of the series all the bonding d-states are filled and the anti-bonding states are empty. The bond strengths are then a maximum. Further filling of the d-states results in the occupation of anti-bonding d-states, which reduces the bond strengths. Consequently in the second half of the transition metal series the cohesive energy, bulk modulus and melting point all decrease as the d-states are filled further.

Notice the remarkable consistency between the changes of crystal structure as we cross the 4d and 5d series: HCP $\rightarrow$ BCC $\rightarrow$ HCP $\rightarrow$ FCC. This is a much more subtle trend because the differences between the energies of these crystal structures are much smaller than the cohesive energies. Nevertheless, it turns out they are directly related to the filling of the d-states.

Once the d-states are all filled they no longer contribute to cohesion because there are as many occupied bonding d-states as occupied anti-bonding d-states. The noble metals copper, silver and gold have full d-states and their cohesion originates from the occupation of s- and p-states - we are back to
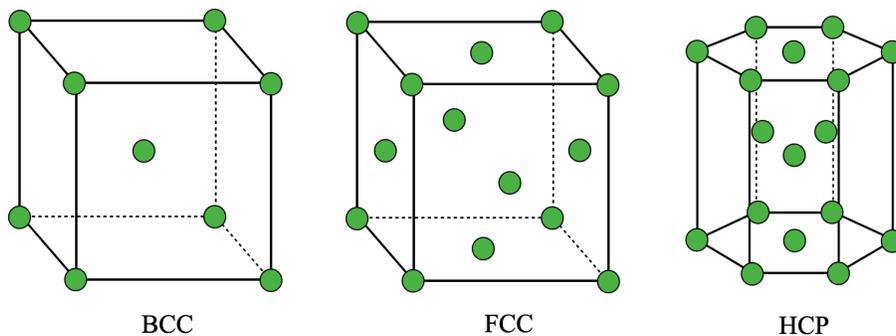
Figure 6: Common crystal structures of metals: body centred cubic (BCC), face centred cubic (FCC) and hexagonal close packed (HCP).

the nearly free electron model.

This raises an important conceptual question. Can nearly free electron metals be described by molecular orbitals comprising linear occupations of atomic states? The answer is yes they can, at least in principle. The electronic states of a nearly free electron metal can also be viewed as giant molecular orbitals consisting of linear combinations of atomic states. The only difference between transition metals and nearly free electron metals is the limited overlap between neighbouring atomic d-states in transition metals compared to the larger overlap between neighbouring atomic s- and p-states in free electron metals. In both cases electrons are itinerant and bonding is unsaturated. The metallic bond in both simple metals and transition metals is an unsaturated covalent bond.

5 Why are metals conductors and insulators non-conductors?

I have argued there is no fundamental difference between a metallic bond and a covalent bond. Bonds in covalent solids and in metals exist through the sharing of electrons. Covalent bonds, like those in alkanes and diamond, are strong, directional and saturated. Metallic bonds in transition metals are also strong and directional but they are unsaturated. Metallic bonds in simple metals tend to be weaker, less directional and they are also unsaturated.

In the chemist's picture of saturated bonding in a covalent insulator there are two electrons localised in the bond between each pair of atoms. In the physicist's picture all occupied delocalised molecular states contribute to the saturated covalent bond between each pair of atoms in the insulator. These two pictures are mathematically and physically equivalent. It is a matter of taste as to which picture we choose. But if the electrons in a covalent insulator are delocalised why don't they conduct electricity like the delocalised electrons in a metal?

We have already encountered the Pauli exclusion principle. It states that no two electrons can be in the same quantum state. The exclusion principle explains the filling of electron states in atoms (the 'aufbau' principle) and it underpins the structure of the Periodic Table. It also plays a central role in many of the properties of electrons in solids.

In particular when an electric field is applied a current will flow only if there are unoccupied electron states available for the electrons to occupy. In metals and insulators there are higher energy states into which electrons can be excited. The difference between them is the amount of energy required for the excitation. In a metal it is practically zero. In an insulator it is a finite amount of energy, called the band gap E_g. The band gap is the difference between the energies of the highest occupied state and the lowest unoccupied state. The existence of a band gap renders an insulator unable to conduct electricity at absolute zero. At finite temperatures the conductivity of an insulator becomes finite because electrons can be excited thermally across the band gap. But it is still extremely small if E_g is large, as in diamond. The thermal excitation of electrons across the band gap is why the electrical

resistance of insulators decreases with temperature.

Why is there a finite band gap in covalent insulators between occupied and unoccupied electron states? One answer is based on the periodic structure of a crystal. The periodicity of a crystal led to the development of band theory. Electronic states in a crystal are in bands of energies. Within a band the energy difference between successive states is so small it is effectively zero. Bands may be separated by a finite amount of energy (this is the band gap E_g) or they may overlap in energy. When a band is partially filled by electrons we have a metal because there is practically no energy barrier to excite electrons to higher energy states. If the highest occupied band is full and separated by a band gap from the lowest unoccupied band we have an insulator. That is the story of metals and insulators according to band theory.

Crystalline pure silicon is an insulator at absolute zero. According to band theory its outermost s- and p-electrons occupy a full band separated by a band gap of 1.1 eV from a higher energy empty band. From a chemist's viewpoint the outermost s- and p-electrons on each atom form saturated bonds to each of its four neighbours at the vertices of a tetrahedron. If an electron in a saturated bond is to be excited it must enter an anti-bonding state. In silicon the anti-bonding states are in a separate higher energy band. The band gap in silicon is then the minimum energy required to excite an electron in a saturated bond into an anti-bonding state[15].

The great advantage of the chemist's local viewpoint is that it is equally applicable to non-crystalline 'amorphous' silicon. In amorphous silicon each atom has saturated bonds to four neighbours at the vertices of a slightly distorted tetrahedron. The distortions are essentially random and the atomic structure is not periodic. The energies of electrons still occur in bands but they can no longer be explained by a theory that assumes a periodic atomic structure. However, a similar argument based on local chemical bonding can be made for the existence of a band gap in amorphous silicon as in crystalline silicon. The origin of the band gap in non-crystalline and crystalline covalent insulators is the same: it is the finite energy required to excite an electron in a saturated bond into an anti-bonding state. Periodicity is not essential either for bands or band gaps.

6   Conclusion

Jeremy Burdett, former Head of the Department of Chemistry at the University of Chicago, wrote the following in his book *Chemical bonding in solids*:

The metallic bond . . . , prevalent in modern day texts, is replaced by a definition of a metal that is just a solid with a partially filled energy band. Metallic bonding per se has disappeared and we suggest that the term be removed from the vernacular.

The metallic bond is just an unsaturated covalent bond. I hope future authors of text-books on chemistry and physics for students in secondary and tertiary education are persuaded that the metallic bond is not a distinct class of chemical bond.

Acknowledgements

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[15]This is unlike the transition metals where bonds are unsaturated, as discussed in section 4. Wherever they occur in the d-band, electrons in the highest occupied states may be excited into unoccupied states without having to cross a band gap.

Further reading

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