

II. Electronic Transport in Materials

Electrical conductivity coefficients σ_{ij} constitute a second-rank tensor relating current density components J_i to electric field E_j : $J_i = \sigma_{ij} E_j$. Cubic crystals and amorphous solids have the same conductivity in all directions so that σ is a scalar property. Tetragonal, hexagonal and trigonal crystals have two independent coefficients measured parallel and perpendicular to the major symmetry direction (c -axis). Three coefficients are required for lower symmetry crystals.

Materials with ionic, covalent or mixed ionic-covalent bonding are normally either insulators or semiconductors. Most useful semiconductors, including Si, Ge, and GaAs, have predominantly covalent bonding. From a practical viewpoint, materials may be classified according to conductivity as metals ($\sim 10^6$ to $10^8 \Omega^{-1} - m^{-1}$), semiconductors ($\sim 10^5$ to $10^{-7} \Omega^{-1} - m^{-1}$), and insulators ($\sim 10^{-8}$ to $10^{-20} \Omega^{-1} - m^{-1}$). Few other physical properties cover such a wide range, which is even wider if superconductors are included. Another important distinction between metals and non-metals is that the conductivity of a metal decreases with increasing temperature while the conductivity of semiconductors and insulators increases with increasing temperature. The band theory of solids provides an explanation of the conductivity values and the temperature dependence.

1. Atomic Orbitals, Molecular Orbitals, and Energy Bands

The energy bands of a solid can be derived from the atomic energy levels of the separated atoms. The high electrical conductivity of alkali and alkaline earth metals can be explained by this model, as can the insulator characteristics of ionic salts and inert-gas crystals. But molecular orbital theory is needed for solid H_2 and other molecular crystals. The atomic orbital treatment fails to predict the vast difference in conductivity between diamond and graphite.

Metals are characterized by partially filled electron bands. Under these conditions an electric field promotes electrons to unfilled states favoring the movement of electrons in the direction antiparallel to the field. The large number of conduction electrons and available states are responsible for the high electrical conductivity of metals. Insulators

possess filled valence bands and empty conduction bands. In a semiconductor, the filled band and empty band are separated by a relatively small band gap. Thermal excitation elevates electrons across the energy gap, leaving behind vacant states in the valence band. Both electrons and holes contribute to conduction.

Linear combinations of atomic orbitals (L.C.A.O.) provide a useful starting point in describing the electronic structure of solids. Electronic wave functions in the crystal are visualized as a superposition of the atomic wave functions centered at the atom sites. The basic idea is to find molecular orbitals made up of linear combinations of atomic orbitals which thereby minimize the energy.

The wave function Ψ for a diatomic molecule is given by

$$\Psi = K_1 \Psi_1 + K_2 \Psi_2,$$

where Ψ_1 and Ψ_2 are atomic wave functions, and K_1 and K_2 are coefficients to be determined by minimizing the energy E . For real wave functions,

$$\begin{aligned} E &= \frac{\int \Psi H \Psi dV}{\int \Psi^2 dV} \\ &= \frac{(K_1 \Psi_1 + K_2 \Psi_2) H (K_1 \Psi_1 + K_2 \Psi_2) dV}{\int (K_1 \Psi_1 + K_2 \Psi_2)^2 dV} \\ &= \frac{K_1^2 \int \Psi_1 H \Psi_1 dV + K_1 K_2 \int \Psi_1 H \Psi_2 dV + K_2 K_1 \int \Psi_2 H \Psi_1 dV + K_2^2 \int \Psi_2 H \Psi_2 dV}{K_1^2 \int \Psi_1^2 dV + 2 K_1 K_2 \int \Psi_1 \Psi_2 dV + K_2^2 \int \Psi_2^2 dV} \end{aligned}$$

It is obvious that $\int \Psi_1 H \Psi_2 dV = \int \Psi_2 H \Psi_1 dV$ since it makes no difference which atom is Number 1. Number 2 tries just as hard. To facilitate manipulation, we use the abbreviations

$$\begin{aligned} H_{ij} &= \int \Psi_i H \Psi_j dV, \\ S_{ij} &= \int \Psi_i \Psi_j dV. \end{aligned}$$

The energy equation becomes

$$E = \frac{K_1^2 H_{11} + 2 K_1 K_2 H_{12} + K_2^2 H_{22}}{K_1^2 S_{11} + 2 K_1 K_2 S_{12} + K_2^2 S_{22}}.$$

If the atomic wave functions Ψ_1 and Ψ_2 are normalized, then $S_{11} = S_{22} = 1$. To minimize E , we set $\partial E / \partial K_1 = 0$, obtaining the relation

$$K_1 (H_{11} - E S_{11}) + K_2 (H_{12} - E S_{12}) = 0. \quad (1)$$

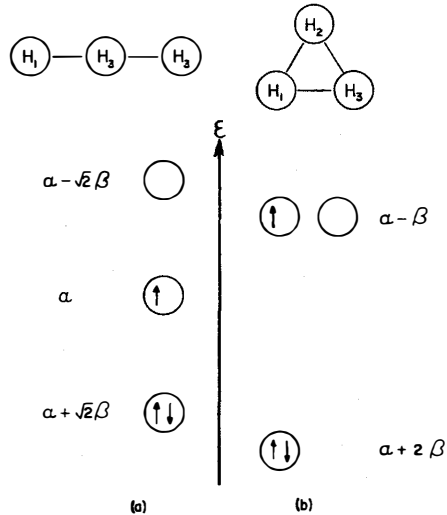


Fig. 8a and b. LCAO energy level scheme for two possible configurations of the H_3 molecule. As explained in the text, α is the coulomb integral and β the resonance integral. The triangular configuration of H_3^+ is predicted to be more stable than the linear state. However, the reverse order is suggested for H_3^- . The triangular and linear configurations have nearly equal energy for the neutral H_3 molecule

Setting $\partial E / \partial K_2 = 0$ leads to

$$K_1(H_{12} - ES_{12}) + K_2(H_{22} - ES_{22}) = 0. \quad (2)$$

The secular Eqs. (1) and (2) are usually written as a determinant,

$$\begin{vmatrix} (H_{11} - ES_{11}) & (H_{12} - ES_{12}) \\ (H_{12} - ES_{12}) & (H_{22} - ES_{22}) \end{vmatrix} = 0.$$

The procedure is to solve the determinant for the energies E after evaluating the integrals H_{ij} and S_{ij} for a given molecular configuration. The calculation is repeated for other possible configurations, comparing energies to find the most stable form. Wave functions of the molecular orbitals are obtained by substituting the energies E in the secular equations, solving for K_1/K_2 , and then normalizing.

To show how the method works, consider the triatomic molecule H_3 . Two possible configurations are the linear $H-H-H$ molecule and the equilateral triangle molecule (Fig. 8). We calculate and compare energies

for the two configurations. For a triatomic molecule, the molecular orbital wave functions

$$\Psi = K_1 \Psi_1 + K_2 \Psi_2 + K_3 \Psi_3$$

lead to the secular determinant

$$\begin{vmatrix} (H_{11} - ES_{11}) & (H_{12} - ES_{12}) & (H_{13} - ES_{13}) \\ (H_{12} - ES_{12}) & (H_{22} - ES_{22}) & (H_{23} - ES_{23}) \\ (H_{13} - ES_{13}) & (H_{23} - ES_{23}) & (H_{33} - ES_{33}) \end{vmatrix} = 0.$$

Methods for evaluating the coulomb integrals (H_{ii}), the resonance integrals (H_{ij}) and the overlap integrals (S_{ij}) are given in the literature. Numerical values have been tabulated for the atomic orbitals occurring commonly in organic molecules [1].

For linear triatomic hydrogen (Fig. 8a), the coulomb integrals $H_{11} \cong H_{22} \cong H_{33} = \alpha$, a negative number representing the energy of the hydrogen 1s electron in the field of a hydrogen nucleus. The resonance integral $H_{12} = \beta$ is also negative, and represents the energy of an electron moving in the fields of Atoms 1 and 2. By symmetry, $H_{23} = \beta$ also. The remaining resonance integral H_{13} is negligibly small because Atoms 1 and 3 are far apart. For the overlap integrals, we make the simplifying assumption that the atoms are far apart so that $S_{12} = S_{13} = S_{23} = 0$. Normalized wave functions give $S_{11} = S_{22} = S_{33} = 1$. Substituting in the secular determinant and solving for energy gives the three roots $E = \alpha$, $\alpha \pm \sqrt{2}\beta$. Each molecular orbital can be occupied by two electrons of opposite spin. The electronic energy of the ground state (Fig. 8) is therefore $(\alpha + \sqrt{2}\beta) + (\alpha + \sqrt{2}\beta) + \alpha = 3\alpha + 2\sqrt{2}\beta$.

Repeating the calculation for triangular H_3 , the only major change is that all hydrogens are now near neighbors. This means that $H_{12} = H_{13} = H_{22} = \beta$. Assuming the other coefficients remain unchanged, the secular determinant gives energies $\alpha + 2\beta$, $\alpha - \beta$, $\alpha - \beta$. For three electrons the ground state energy is $(\alpha + 2\beta) + (\alpha + 2\beta) + (\alpha - \beta) = 3\alpha + 3\beta$, which is slightly more stable than the linear case. Note that triangular configuration is also more stable for the H_3^+ ion but not for H_3^- .

For a crystal containing N atoms, a band of $2N$ closely-spaced energy levels develops from each atomic orbital. The width of the band depends on the overlap between atomic wave functions. Tightly bound inner orbitals give rise to narrow bands whereas the bands formed by valence orbitals are relatively wide. Electron mobility increases with band width.

Energy band structures of He, Li and Be are illustrated in Fig. 9. Helium atoms possess two electrons which generally fill the 1s shell. The

1s level lies far below 2s so that there is no overlap between the bands in solid helium. The 1s valence band is completely full and the 2s conduction band is empty, making helium an excellent insulator. Lithium has one more electron than helium. The additional electrons enter the 2s band, filling it half-way, so that lithium is a metal. Beryllium is also a metal because of the overlap between the 2s and 2p orbitals. The broadening of bands is sufficient to overcome the small separation of 2s

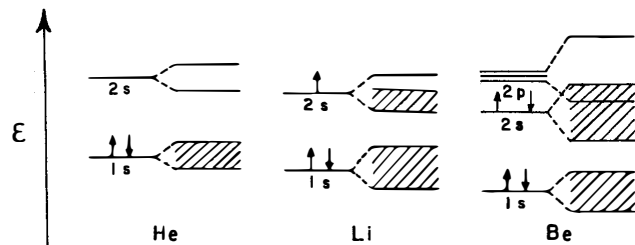


Fig. 9. Energy band structures for He, Li, and Be. Helium is an insulator while lithium and beryllium are metals with partly-filled conduction bands

and 2p levels. Other alkali and alkaline earth elements behave analogously to lithium and beryllium. The electronic structure of ionic crystals can also be derived from atomic orbitals. Rocksalt consists of Na^+ and Cl^- ions with a fully-occupied valence band formed from the 3p levels of Cl. The empty 3s states of the sodium ions combine to form the conduction band. Like most ionic salts, NaCl is transparent, indicating that the band gap exceeds several electron volts.

The atomic orbital approach leads to erroneous conclusions for molecular crystals. Hydrogen has but one electron so that the 1s band is only half-filled in solid hydrogen. Crystalline hydrogen is an insulator but according to this picture, it should be a good conductor. Molecular orbitals provide a more accurate description since solid hydrogen contains H_2 molecules held together by weak van der Waals forces. For a crystal of N hydrogen molecules ($2N$ atoms), there are N bonding orbitals, one for each molecule. The N orbitals combine to form an N -level $\sigma(1s)$ band in the crystal. In a similar way, the antibonding orbitals form an N -level $\sigma^*(1s)$ band. Both bands are relatively narrow since the interactions between molecules are rather weak. Therefore there is no overlap between bands (Fig. 10) and solid hydrogen is an insulator.

Carbon occurs in nature in two polymorphic forms. Diamond has a very high electrical resistivity, while graphite is an anisotropic semi-metal. The conductivity of graphite is greatest in directions parallel to the graphite layers.

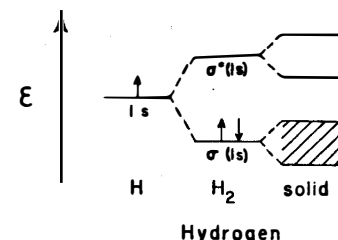


Fig. 10. Molecular-orbital energy band structure for hydrogen. Solid hydrogen is an insulator containing H_2 molecules

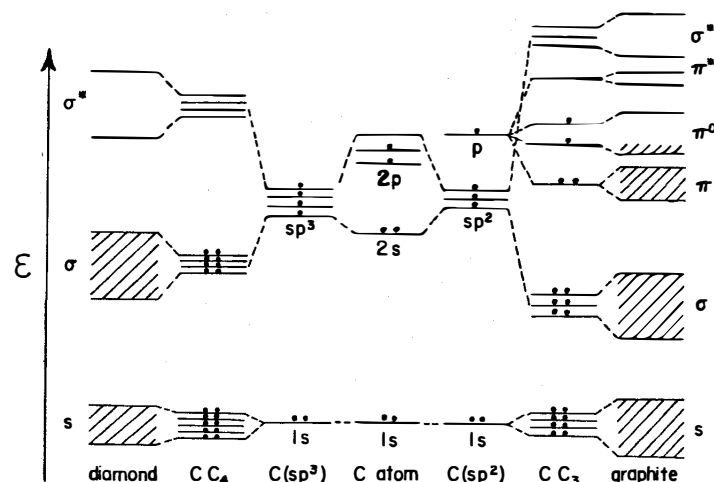


Fig. 11. Energy level diagrams for diamond and graphite showing how the bands are derived from atomic and molecular orbitals. Diamond has a wide gap between the conduction and valence bands, while graphite is a good conductor because of the partly-filled conduction band

In diamond each carbon atom is bonded to four other carbons arranged in tetrahedral fashion. The 2s and 2p electrons combine to form sp^3 hybrid orbitals. For each CC_4 tetrahedral group there are four sp^3 orbitals associated with the central carbon, and one with each neighbor, forming four electron pair bonds (σ bonds). The four electrons from the central carbon and one from each neighboring carbon are just sufficient to fill the σ orbitals. The four antibonding σ^* orbitals are empty. In diamond, the σ and σ^* orbitals form the valence and conduction bands, and are separated by a sizeable energy gap. Hence diamond is an insulator, as illustrated in Fig. 11.

A different type of bonding occurs in graphite. Each carbon is bonded to three near neighbors in the graphite layer by sp^2 hybrids and by p_π orbitals. A CC_3 fragment of the structure contains three $\sigma(sp^2)$ bonding orbitals, three σ^* orbitals, and four π orbitals: one π bonding orbital, one π^* antibonding orbital, and two degenerate π° non-bonding orbitals. The ten electrons associated with such a group fill the σ and π orbitals and half the π° orbitals. Thus in graphite there is a partially-filled band, explaining its metallic characteristics. There is more overlap between orbitals for atoms in the same plane because of the shorter interatomic distances. Hence the bands are wider and the mobility greater for conductivity parallel to the graphite layers [2].

2. Electronic Materials

Electron transport is important in semiconductors and other electronic materials. Solid-state electronics is centered about the classical elemental semiconductors silicon and germanium which crystallize in the diamond structure (Fig. 12). Each atom forms electron-pair covalent bonds to four nearest neighbors. Because of their importance and unusual chemical characteristics, it has been possible to prepare Si and Ge at impurity levels below 10^{-7} , a purity never achieved with other synthetic materials. Crystal perfection is correspondingly high, with large dislocation-free crystals a practical reality. Extensive experimental and theoretical studies led to the unprecedented situation where basic theory overtook technology. A detailed understanding of energy bands, effective masses, and electron interactions with impurities and phonons led to the prediction of numerous semiconductor devices (including the field-effect transistor) long before processing techniques were developed. Since the discovery of the transistor in 1948, materials technology has been the slow step in device development. Break-throughs in zone-refining, the preparation of surfaces, planar diffusion processes, epitaxy, and evaporation techniques were significant advances leading to the amazing integrated circuits of today.

Compound semiconductors have been of immense interest in the past twenty years despite the formidable materials problems. Elements positioned symmetrically about Group IV are generally used in compound semiconductors. GaAs (III-V), ZnS (II-VI), and SiC (IV-IV) are representative of a class of materials finding applications at higher speeds, higher power, higher frequencies and higher temperatures than Si and Ge. Gallium arsenide varactor diodes and oscillators operate well in the microwave region, one of the innovations in radar technology

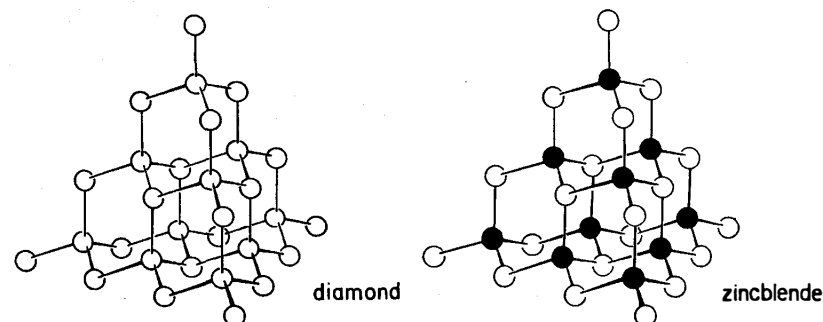


Fig. 12. In the diamond structure every carbon atom is tetrahedrally bonded to four neighboring carbon atoms. The zincblende structure is derived from that of diamond by replacing alternate atoms with zinc and sulfur. Most semiconductors of commercial importance are isomorphous with diamond or zincblende

required for automobile radar. Narrow band gap semiconductors such as indium antimonide are used in Hall effect devices and as infrared detectors. Electroluminescent diodes and alpha-numeric devices made of silicon carbide are being mass-produced in Russia. Yet compared with silicon and germanium, compound semiconductors have made little impact in solid state electronics. In addition to the usual materials problems of purity and crystal perfection, the equally difficult problem of stoichiometry must be surmounted.

In the next decade development work will center on integrated circuit technology of the hybrid and monolithic varieties. Production targets of 10^4 components per chip area of one square millimeter can be surpassed by refinement of present-day technology. Both classical p-n junctions and metal-oxide-semiconductor (MOS) devices will find uses in the two giants of the electronic world, entertainment and computers.

Only silicon will be used in integrated circuits in the foreseeable future. Si is preferred over Ge because germanium oxide does not have the stability and insulating characteristics of silicon oxide.

Semiconductor devices for handling high levels of electric power will also proliferate in the years ahead. Solid state alternators are now being used in automobiles. Increased use of semiconductor devices for switching extremely high power, either in motors or in power transmission, will require refinements of present technology. Silicon will continue to be the principal semiconductor material, though silicon carbide is probably more suitable for power control.

3. Semiconductors

The prediction of new semiconductor compounds and their properties is of great interest because of their importance to the electronics industry. In particular, the questions to be answered are these. Given the chemical composition and structure, is it possible to predict whether the material is a semiconductor or not? And second, how do the important properties, such as band gap and mobility, depend on crystal chemistry?

The invention of the transistor in 1948 initiated a search for compounds similar to silicon and germanium. In 1952 came the III-V compounds such as GaAs, followed by a host of others. Physicists have tended to emphasize the importance of band theory calculations in explaining semiconductor properties, but the calculations are complex, and it is impossible to survey large numbers of materials in this way. Simpler relations are needed, concepts like that of the semiconducting bond proposed by MOOSER and PEARSON [3]. Germanium and silicon consist of a continuous network of covalent bonds in which the shared electrons lead to filled valence subshells. In semiconductor compounds the cations are seldom in contact, so that only the anions need acquire filled shells. Any bonds formed between cations with partly filled shells must be localized, and not extend throughout the crystal.

The difference between semiconductors and metals therefore relates to the filling of valence shells. Differences between insulators and semiconductors are not clear cut because an insulator is simply a semiconductor with a wide band gap. Insulators become semiconductors at high temperatures where electrons in the valence band acquire sufficient thermal energy to gain promotion to empty in the conduction band. The two most important classes of insulators are ionic compounds and molecular solids.

MOOSER and PEARSON have given a formula which can be used to predict semiconductors. Semiconductor compounds satisfy the relation

$$\frac{n_e}{n_a} + N_a - N_c = 8, \quad (1)$$

where n_e is number of valence electrons per formula unit, n_a is the number of anions per formula unit, N_a is the average number of anion-anion bonds, per anion, and N_c is average number of cation-cation bonds formed by each cation. n_e and n_a are obtained from the chemical composition, and N_c and N_a determined from the structure. A number of illustrations are given in Table 5.

Some of the examples listed require further comment. The elements Ge, As, and Se point up the similarity between the 8- N rule and the

Table 5. Representative semiconductors satisfying the Mooser-Pearson relation

Compound	n_e	n_a	N_a	N_c	$\frac{n_e}{n_a} + N_a - N_c$
Ge	4	1	4	0	8
As	5	1	3	0	8
Se	6	1	2	0	8
SiC	8	2	4	0	8
GaAs	8	1	0	0	8
CdTe	8	1	0	0	8
AgInTe ₂	16	2	0	0	8
PbS	8	1	0	0	8
Mg ₂ Sn	8	1	0	0	8
LiMgSb	8	1	0	0	8
Li ₃ Bi	8	1	0	0	8
Mg ₃ Sb ₂	16	2	0	0	8
Bi ₂ Te ₃	24	3	0	0	8
Fe ₂ O ₃	24	3	0	0	8
BaTiO ₃	24	3	0	0	8
FeS ₂	14	2	1	0	8
CdSb	7	1	1	0	8
GaTe	9	1	0	1	8

Mooser-Pearson relation. The 8- N rule is used to predict the number of valence bonds formed by an element in the N th column of the periodic system. For example, selenium in Column VI forms $8 - 6 = 2$ valence bonds, as observed in both the ring and helical forms. According to the Mooser-Pearson relation, selenium is a semiconductor because it forms electron-pair bonds with two near neighbors, and in this way every atom acquires a filled shell, and every electron participates in bonding. High electrical conductivity (metallic behavior) occurs in compounds in which not all of the valence electrons are involved in bonding.

The importance of cation-cation and anion-anion bonds is apparent in GaTe, FeS₂, and CdSb (Table 5). Gallium telluride forms a layer-like structure with one short Ga-Ga bond per gallium. Gallium would normally contribute three valence electrons to the anion, but one electron is involved in an electron-pair bond with another cation, leaving two for each tellurium atom. Thus the anion electron shell is filled with eight electrons and GaTe is a semiconductor. Anion-anion bonds occur in FeS₂ and CdSb. Cadmium antimonide has a very deformed diamond arrangement in which Sb is coordinated to three Cd and one Sb, all near 2.8 Å. From the structure it is therefore reasonable to postulate that an Sb-Sb bond is formed, allowing the anions to satisfy their valence requirements. Pyrite is a better example of anion-anion bonds. The FeS₂ structure contains Fe²⁺ ions and S₂²⁻ groups.

New semiconducting compounds can be derived from known examples by a process of cross-substitution, replacing one element by pairs from other columns of the periodic system while keeping the valence-electron to atom ratio constant. The III-V and II-VI compounds based on the Column IV semiconductors are familiar examples. The substituting process can be carried several steps further. The semiconductor AgInTe_2 is derived from CdTe by substituting equal amounts of monovalent silver and trivalent indium for divalent cadmium. Successive substitutions in the cation sublattice leads to $\text{Ag}_2\text{CdSnTe}_4$ and $\text{Ag}_5\text{InSn}_2\text{Te}_8$. Cation vacancies occur in semiconducting In_2Te_3 and HgIn_2Te_4 . Substitutions need not be confined to the cation sublattice; cross-substitution involving the anion sublattice, or both sublattices are also possible. Symmetric substitutions in the anion sublattice occurs in Al_2CO , a derivative of AlN . Double substitution takes place in LiMgSb , a semiconductor derived from Mg_2Sn by replacing half of the cations and all the anions. Similar derivative structures occur in nature. The minerals zincblende (ZnS), chalcopyrite (CuFeS_2), and stannite ($\text{Cu}_2\text{FeSnS}_4$) are three minerals in such a series.

Many semiconductors have structures based on close-packed anion arrays. The zincblende structure and its derivatives are good examples (Fig. 12). Phases in which cations occupy tetrahedral interstices and satisfy Eq. (1) are semiconductors, almost without exception, but this is not true for cations in octahedral coordination in a close-packed anion lattice, even if their compositions seemingly satisfy Eq. (1). This is because octahedral coordination is frequently found in materials with metallic or ionic bonding.

In attempting to relate crystal structure to semiconducting behavior, one must be careful not to overestimate the importance of long range order. The existence of non-crystalline semiconductors such as amorphous and liquid selenium show that long range order is unnecessary. Solid state devices have been fabricated from amorphous semiconductors to act as threshold switches and as memory devices which can be activated either optically or electrically. The biggest application is in xerography, where glassy selenium and arsenic-selenium mixtures are used as the photoconductive element on the drum that produces the copy.

Amorphous memory devices appear to offer special advantages. Being already disordered, non-crystalline materials are highly resistant to radiation. The second advantage is that glassy devices do not require power to retain stored information and can be interrogated nondestructively.

Many semiconductors are excellent photoconductors as well, with large decreases in resistance under illumination. Photoconductors such as selenium retain charge in the dark, but wherever the photoconductor

is exposed to light the charge disappears. In the Xerox process, glassy selenium is placed on a drum and uniformly charged by corona-produced ions. A bright light illuminates the original drawing, and a lens focuses the image on the Se-covered drum. Charge drains away where the light strikes. Elsewhere the charge remains and a special dust is applied which adheres to the charged regions of the image. The image is then transferred electrostatically from drum to paper, and fused to the paper by rapid heating.

4. Band Gap and Mobility

A number of relations between band gap and structure have been proposed, most of them empirical. Band gaps of III-V compounds are larger than the corresponding Column IV elements: AlP has a larger gap than Si , GaAs exceeds Ge , and InSb is greater than Sn . From examples such as these, relations between electronegativity differences and E_g have been established. Ionic compounds have greater E_g values than most covalent compounds. To illustrate how the band gap can be adjusted, consider two examples mentioned earlier. Comparing CdTe and its derivative AgInTe_2 , we note that electronegativity differences to the three bonds are in the order $\text{Ag-Te} > \text{Cd-Te} > \text{In-Te}$, with the latter being the weakest bond. Energy gap is determined by the weakest bond since it has the smallest interband separation. Therefore this type of cross-substitution usually lowers E_g . The energy gap is 0.96 eV for AgInTe_2 and 1.5 eV for CdTe . In the second example, LiMgSb is derived from Mg_2Sn , increasing E_g , because electronegativity differences are in the order $\text{Li-Sb} > \text{Mg-Sb} > \text{Mg-Sn}$.

The electronegativity scale not only provides a measure of the bonding type but is also useful in predicting physical properties. An empirical relation between electronic band gap and electronegativity is shown in Fig. 13. Band gaps range from a fraction of an electron-volt in certain semiconductors to several eV in good insulators.

The band gap E_g of a semiconductor is important in determining its electrical conductivity σ ,

$$\sigma \sim \mu e^{-E_g/kT}$$

where the mobility μ depends chiefly on imperfections and temperature. When the band gap is comparable to thermal energies ($kT \sim 1/40$ eV at room temperature), large numbers of electrons are promoted from the valence to the conduction band, greatly increasing the electrical conductivity. Among compound semiconductors E_g increases with ionicity as shown in Fig. 13. Ionic compounds show a large band gap and optical

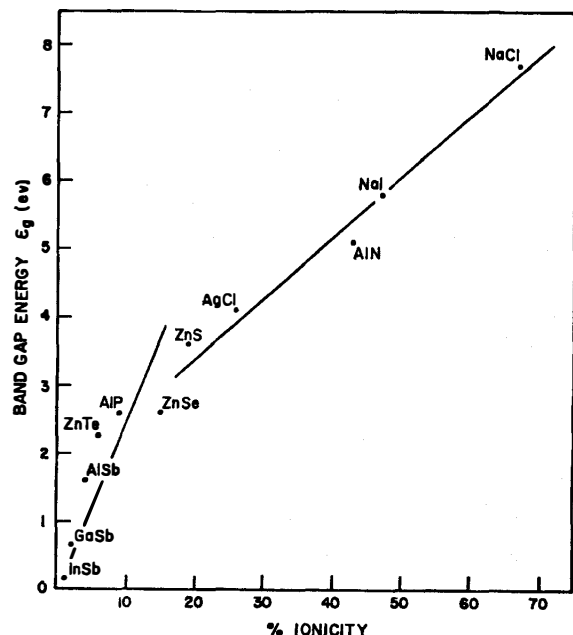


Fig. 13. Band gap generally increases with ionicity. The more ionic compounds with the rocksalt structure usually have wider band gaps than covalently bonded materials with the zincblende structure

transparency extending well into the ultraviolet region, whereas most covalent semiconductors are either opaque or colored because of their narrow band gaps. As ionicity increases, electrons are more tightly bound to the cores with a greater degree of localization of charge carriers.

Mobility is very sensitive to imperfections so that most experimental measurements are more indicative of crystal growth technique than intrinsic limitations. Experimental mobility values for undoped Si and Ge have increased over the years as better crystals have been grown.

In pure materials free from defects, mobility is determined by the effective mass interaction with lattice vibrations. Heavy masses reduce the latter, decreasing the scattering by lattice vibrations and contributing to the large mobilities ($> 10000 \text{ cm}^2/\text{V-sec}$) found in HgTe and InSb. Compounds with highly ionic bonding have extremely low mobilities, both electrons and holes. When the electronegativity difference is greater than 1 unit, mobilities greater than $1000 \text{ cm}^2/\text{V-sec}$ are unlikely.

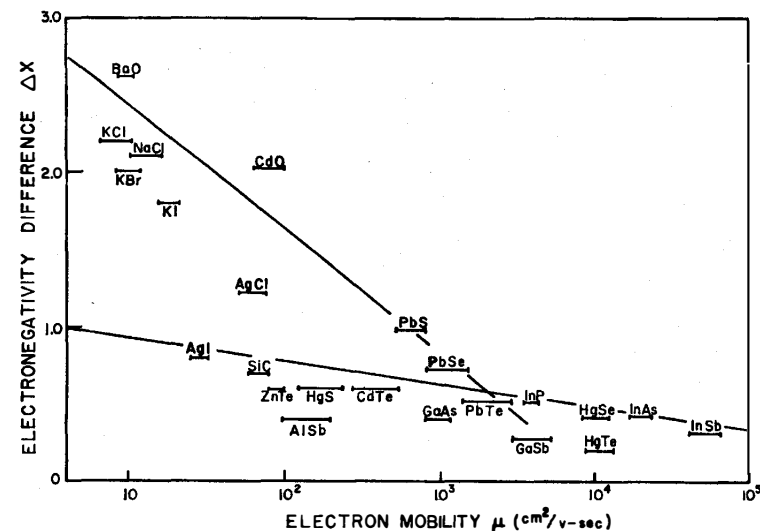


Fig. 14. Correlation between the electron mobility and the electronegativity difference of some zincblende and rocksalt type compounds [5]

Generally mobilities increase with molecular weight and decrease with electronegativity difference (Fig. 14). The explanation lies in the polarization effect of mobile electrons or holes on the surrounding atoms. The motion of charge carriers is accompanied by an adjustment in position of the ions which is intrinsically slow. Coulomb coupling between charge carriers and ions occurs in ionic compounds.

5. Semiconductor Doping

Chemical impurities are used to control the conductivity σ of semiconductors, $\sigma = n\mu_e + p\mu_h$. The density of conduction-band electrons and valence-band holes are n and p , with mobilities μ_e and μ_h . For wide band gap materials near 1 eV or larger, the room-temperature carrier concentrations are controlled by doping. Donor atoms contribute electrons to the conduction band, and acceptor atoms remove electrons from the valence band, leaving holes behind. Donor (D) and acceptor (A) levels in germanium are shown in Fig. 15. The dopants illustrated are substitutional impurities which replace Ge in the diamond-like structure (Fig. 12). Germanium has the electron configuration $3d^{10}4s^24p^2$. The

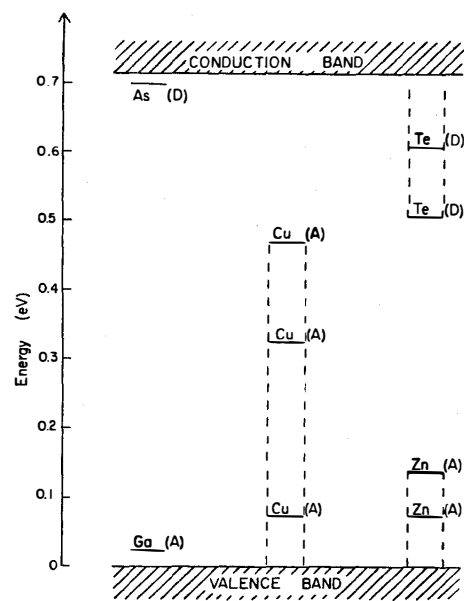


Fig. 15. Energy levels for acceptor A and donor D impurities in germanium

four outer electrons form tetrahedral sp^3 hybrid bonds to four neighboring germanium atoms in the crystal. Substitutional impurities with more than four outer electrons tend to be donors because only four electrons are needed for bonding. The remaining electrons can be ionized away to the conduction band if the temperature is high enough.

The Bohr model for the hydrogen atom has been used to predict donor and acceptor energy levels:

$$E = \frac{m^* e^4}{8 K^2 \epsilon_0^2 h^2} [\text{MKS}].$$

m^* is the effective mass, e the electronic charge, K the dielectric constant, h Planck's constant and ϵ_0 the permittivity of free space. Predicted values of 0.01 eV for Ge and 0.05 eV for Si are in reasonable agreement with Group III acceptor levels in the two materials.

Cobalt, nickel and most other transition elements have an outer electron configuration $4s^2$ and therefore give rise to two acceptor states in Ge. The d electrons play no role. Deep-lying states like those of copper

can be troublesome in semiconductor devices. Trapping and recombination occur at these sites, reducing the lifetimes of minority carriers.

Many elements do not substitute for Si or Ge because of size mismatch. Small atoms such as hydrogen enter interstitial sites and are not electrically-active.

Impurity atoms also effect the mobility. The coulomb fields associated with ionized impurities exert forces on charge carriers, tending to scatter them and reduce the mobility. Defects and disorder also reduce mobility.

Columns V and VI elements are donors whereas Column III, Column II, and transition-metal elements tend to be acceptors. Gallium, a Column III element, requires one additional outer electron to form four covalent bonds. An electron is thermally-excited to this acceptor state from a filled state of lower energy, leaving a hole behind. Zinc needs two electrons and copper three, therefore Ga, Zn, and Cu create 1-, 2-, and 3-acceptor states, respectively.

An interesting type of substitutional impurity occurs in natural diamonds. The best blue-white diamonds vary considerably in their optical and electrical properties. Type 1 diamonds show appreciable absorption in the near ultraviolet around 3000 Å, and in the near infrared. Type 2 diamonds show little absorption at wavelengths longer than the 2200 Å band gap cut-off. Type 2 diamonds are useful as radiation detectors, making use of the current pulse created by an ionizing particle. Type 1 diamonds are useless in this regard.

Spectroscopic analyses have shown that diamonds are free from most impurities except nitrogen. Silicon, aluminium, copper, and magnesium are present in amounts less than a few parts per million, and appear to be concentrated in inclusions rather than in the diamond structure. The same is true of Fe and Ni in synthetic diamond. But nitrogen is different. Mass spectroscopy and neutron activation analyses show that N is present up to 1 part in a thousand, and that the UV and IR absorption are proportional to the nitrogen concentration; the latter are C-N vibrations. Nitrogen is also responsible for the difference in electrical behavior, acting as traps which reduce hole mobility to zero.

The peculiar feature of the nitrogen impurities is that it acts like N_2 molecules, rather than individual atoms. Electron spin resonance shows an absence of unpaired spins. Since the density changes little with nitrogen content, it appears that pairs (or even larger groups) of carbons are replaced substitutionally by nitrogen. Since nitrogen is atomic number 7 and carbon is six, the extra electrons seem to be forming $N=N$ double bonds.

Pure transition-metal oxides are generally insulators but deviations from stoichiometry increase the conductivity. In nickel oxide, for example, cation vacancies are created when the crystal is heated near

1000° C, taking up oxygen and partially converting divalent nickel to the trivalent state. Each molecule of oxygen converts four Ni^{2+} to Ni^{3+} and introduces two cation vacancies. In general, however, it is difficult to obtain and control large deviations from stoichiometry by thermal techniques. The limited range of composition and the lack of thermal stability limit the utility of this method.

Verwey and co-workers overcame this difficulty by introducing controlled-valency semiconductors. The $\text{Li}_x\text{Ni}_{1-x}\text{O}$ system illustrates the principle. Monovalent lithium substitutes for nickel, converting some nickel ions to the trivalent state; a more descriptive chemical formula would be $\text{Li}_x^+\text{Ni}_x^{3+}\text{Ni}_{1-2x}^{2+}\text{O}^{2-}$. The excess charge on the trivalent nickel ions is not localized, and in moving from one Ni atom to another, contributes to the electrical conductivity. A 10% substitution of Li lowers the electrical resistivity from $10^{+10} \Omega\text{-cm}$ to $1 \Omega\text{-cm}$. The chemical and thermal stability of such materials is superior to vacancy-induced semiconductors, making them of interest in thermistor devices.

Impurities sometimes increase resistivity rather than lowering it. The addition of iron to lithium nickel oxide results in the formation of $\text{Li}^+\text{-Fe}^{3+}$ pairs so that fewer Ni^{3+} ions are formed. Other foreign ions such as Mg^{2+} block the $\text{Ni}^{3+}\text{-Ni}^{2+}$ electron-transfer mechanism and also raise the resistivity.

6. Semimetals and Narrow Gap Semiconductors

In medieval times Paracelsus referred to bismuth as a "bastard" or "half-metal" because of its brittleness. Such materials in which the valence and conduction band overlap slightly are now called semimetals [6]. Electrons from the top of the valence band spill over into levels of lower energy at the bottom of the conduction band.

Group V elements arsenic, antimony and bismuth are the best known semimetals with band overlaps of 0.50, 0.16, and 0.03 eV respectively. HgS , HgSe , and HgTe with the zincblende structure are also semimetals. Semimetals and narrow band gap semiconductors find uses as Hall and magnetoresistance devices, in thermoelectric and thermomagnetic refrigeration, and as sources and detectors of infrared radiation.

A narrow band gap semiconductor is one in which the energy gap is comparable to kT , 0.025 eV at room temperature. Important examples include InSb (0.23 eV), SnTe (0.2), GeTe (0.1), and the chalcogenides of lead.

In solid solutions the energy gap depends on composition so that semiconductors can be tailor-made by alloying. There is considerable interest in narrow-gap semiconductor lasers and detectors which operate

in the infrared region beyond 10 μm . Single-mode continuous-wave lasers fabricated from lead-tin chalcogenides have several advantages over other lasers. They are small and easily modulated by passing a current through the diode making optical excitation unnecessary, and the frequency can be tuned by adjusting the Pb/Sn ratio.

The energy gaps of PbS , PbSe , and PbTe can be decreased by alloying with the corresponding tin chalcogenide. If SnTe is added to PbTe , the energy gap of the resultant alloy decreases until eventually the valence band and conduction band cross over and exchange roles. The cross-over composition with zero band gap is $\text{Pb}_{0.65}\text{Sn}_{0.35}\text{Te}$. If still more SnTe is added, the gap again gets larger.

Somewhat similar behavior has been observed in the $\text{HgTe}\text{-CdTe}$ system. Mercury telluride is a semimetal while cadmium telluride is a semiconductor. Adding CdTe to HgTe reduces the band overlap until a semimetal to semiconductor transition occurs near $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$. A number of these narrow-gap semiconducting alloys are promising Raman laser materials. Changes in the band edge positions is a characteristic feature of solid solutions of semimetals and narrow gap semiconductors.

7. Magnetic Semiconductors

When a magnetic field is applied to a material, the electrical resistance of the sample changes, an effect known as magnetoresistance. In most materials resistivity increases with magnetic field, since the current effectively follows a longer path, but negative magnetoresistance effects have been observed in magnetic semiconductors. Magnetoresistance devices have been used as variable resistors with the resistance controlled by magnetic flux rather than sliding electrical contacts. Displacement meters and microphones have also been constructed using high-mobility InSb crystals and non-uniform magnetic fields. Semiconductors are generally used for all applications because the effects are much larger than in metals.

Magnetic semiconductors have received increased attention in recent years because of their interesting magnetoresistance and magneto-optical properties. A number of chalcogenide spinels are magnetically-ordered semiconductors. For example, CdCr_2Se_4 is ferromagnetic ($T_c = 130^\circ\text{K}$) and semiconducting ($E_g = 1.2 \text{ eV}$). The full t_{2g} orbitals of Cr^{3+} overlap the valence band in this compound, giving a sharply peaked density-of-states at the top of the valence band. Applied magnetic fields profoundly affect the transport and optical properties, especially near the Curie temperature. Doped with Ga or In, n -type CdCr_2Se_4 exhibits a large

resistivity peak and a giant magnetoresistance affect near 130°K. A field 10 kOe produces a 100% change in resistivity at this temperature [7]. Similar effects are observed in EuS near 17°K. The effects have been attributed to spin-splitting of the energy bands together with spin-disorder scattering.

8. Molecular Circuits

Electronic circuits become smaller and smaller as vacuum tubes are replaced by transistors and integrated circuits. The next step in micro-miniaturization may involve individual molecules as functional electronic components. Two recent proposals suggest how such subminiature circuits might be created. A collective phenomenon called *electromagnetic molecular electronic resonance* (EMER) occurs among the bonding electrons of long chain polymers. If the electron density at the end of a short molecular chain is perturbed for a very short time ($\sim 10^{-15}$ sec), the perturbation may propagate as a wave along the chain. On reaching the end, the charge perturbation will be reflected and oscillate back and forth. Under these conditions, the entire chain would resonate like an antenna in the 10^{13} to 10^{14} Hz range. In addition, the chain could resonate with a series of harmonics up to visible wavelengths. The actual perturbing might be accomplished by inelastic scattering of 5000 Å photons from an ion laser. Circuits might include paramagnetic amplifiers, harmonic generators, oscillators, heterodyne detectors and EMER lasers.

Molecular rectifiers to convert a.c. to d.c. on a superminiature scale have also been suggested. The rectifier would consist of a polar molecule, similar to that shown in Fig. 16. The acceptor end would easily accept an electron, while the donor end would easily give one up. Electrons flowing into the acceptor end would continue along the molecule and be passed on to the remainder of the circuit by the donor end. Current flowing in the opposite direction, however, would be blocked from entering the molecule. To avoid short-circuiting the molecule between donor and acceptor ends, it may be necessary to incorporate an insulating chemical bridge between the two ends. Given the wide range of organic compounds that can now be synthesized, there appears to be no reason why a molecular rectifier cannot be made.

Another recent innovation is the semiconductor superlattice. Man-made superlattices consisting of alternating layers of two semiconductor materials provide a one-dimensional periodic potential of adjustable spacing. Layered structures of GaAs and GaAlAs₂ with periods of 50–100 Å have been fabricated by molecular-beam epitaxial vapor

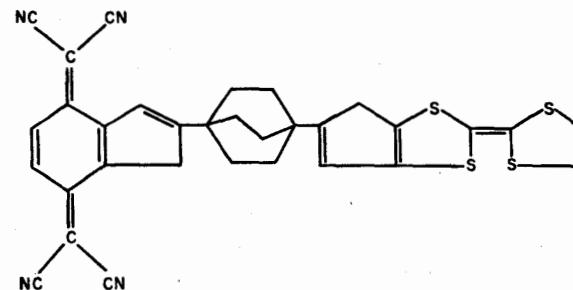


Fig. 16. Possible molecular rectifier with donor and acceptor terminations to convert AC to DC on a very small scale

deposition [8]. If the period of the semiconductor superlattice is shorter than the electron mean free path, strong energy dispersion is effected. Electrons interfere when reflected from the layers, forming a Bloch oscillator which operates at 10^{12} Hz—a frequency difficult to obtain by any other method.

9. Metal-Metal Bonding

In oxides the bonding is nearly always between cation and anion. One of the few exceptions is the metal-metal bonding found in certain transition metal compounds. It appears when metals of normally high valence state are constrained to lower oxidation states. It is believed that *d*-orbitals are used in metal-metal bonding since the metal separation is comparable to orbital size [9].

Evidence for metal-metal bonding includes the following: short metal-metal distances, diamagnetism rather than antiferromagnetism, and in some cases metallic behavior. Examples include VO₂ in which vanadium atoms in neighboring octahedra displace toward one another, and Cs₃Re₃Cl₁₂ with Re₃ clusters again with short *m-m* bonds. In addition to V and Re, compounds of Ti, Nb, Mo, Ta, Zr, Hf, and W show similar behavior. The metal-metal distances are usually near 2.5 Å.

Vanadium dioxide undergoes a metal-semiconductor phase transformation at 68° C with an abrupt change in resistivity from 10^{-5} Ω-cm to 1 Ω-cm. Thin film devices capable of submicrosecond switching times have been proposed [10].

Thick film resistive glazes are widely used in hybrid microelectronic systems. Most of the successful resistor formulations are based on highly

conductive oxides, preferably with low temperature coefficients of resistance. Low current noise and chemical stability during the processing conditions are also desirable. Beginning with the PdO-Ag glaze introduced a number of years ago, the oxides of platinum-family metals have found wide application in the thick film industry [11].

Barium ruthenate is typical of the family. Ceramic specimens of BaRuO₃ are highly conducting ($\rho \sim 10^{-3} \Omega\text{-cm}$) with a positive temperature coefficient indicative of metallic-type conductivity. RuO₆ octahedra share faces in the BaRuO₃ structure bringing ruthenium ions into very close approach. In fact, the Ru-Ru distance for such pairs is 2.55 Å, which is shorter than the separation in ruthenium metal (2.65 Å). This suggests overlap of the cation t_{2g} orbitals, leading to the collective electron d states and metallic conductivity.

10. Anisotropic Conductors

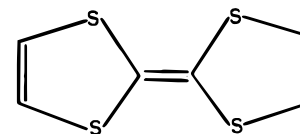
The recent discovery of several one-dimensional conductors has made possible the comparison of experimental results with theoretical predictions. Tetracyanoquinodimethane (TCNQ) salts and mixed-valency planar complexes of platinum such as K₂Pt(CN)₄Br_{0.3} · 3H₂O are the best known examples of pseudo-one-dimensional metals.

Some organic crystals have a maximum electrical conductivity approaching that of metallic copper (Fig. 17). Crystals combining the molecules tetrathiofulvalene and tetracyanoquinodimethane (TTF-TCNQ) have the electrical properties of a metal, yet contain no metallic elements. Though somewhat brittle, the compound sublimates at temperatures as low as 130°C, and resolidifies readily to form thin-film coatings. Conductivity increases from about $10^3 \Omega^{-1}\text{cm}^{-1}$ at room temperature to values exceeding $10^4 \Omega^{-1}\text{cm}^{-1}$ at 100°K. Below 60°K the compound becomes an insulating dielectric. TTF-TCNQ is highly dichroic because the conductivity is very anisotropic. The material polarizes light at near infrared wavelengths, and good polarizers for these frequencies are relatively scarce.

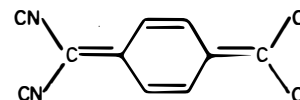
TCNQ molecules stacked face-to-face form linear chains in the TCNQ charge-transfer salts. In NMP-TCNQ, the highly-polarizable donor molecule N-methyl phenazinium transfers an electron to each TCNQ molecule, resulting in a half-filled conduction band with the possibility of metallic behavior along the chains.

The transition metal complexes exhibiting one-dimensional metallic conductivity are mainly limited to nickel, palladium and platinum compounds. The metal atoms are surrounded by a square-planar arrangement of ligands, and the molecular groups are stacked above one

11. Superconductivity



TTF



TCNQ

Fig. 17. Metallic-like TTF-TCNQ crystals contain molecules of tetrathiofulvalene and tetracyanoquinodimethane

another to form a chain of metal atoms in one crystallographic direction. The planar platinum complexes form linear chains of Pt atoms with Pt-Pt distances comparable to those in the pure metal. Partial oxidation results in a stable compound with fractional valency, giving rise to one-dimensional metallic conductivity in the partially-filled d_{z^2} band.

Although the chemistry of the TCNQ salts and the Pt complexes are completely different, the physical properties are similar. At high temperatures, the electrical conductivity is nearly independent of temperature but thermal activation processes become apparent on cooling. A model of interrupted strands offers a simple explanation for the temperature dependence of one-dimensional conductors [12]. The disorder and imperfections in a real crystal are likely causes for such behavior.

11. Superconductivity

In 1908 KAMERLINGH ONNES discovered superconductivity in the element mercury: when immersed in liquid helium, mercury showed no electrical resistance. More than 1000 superconductors have been found since, mostly alloys or intermetallic compounds. Normal metals such as copper or iron exhibit a small but finite resistance at very low temperatures, but about two dozen elements are superconductors at low temperatures.

The superconducting state is characterized by a critical temperature (T_c), a critical field (H_c), and a critical current density (J_c). T_c is the

temperature at which the material transforms from a normal metal to superconducting on cooling. Below T_c , external magnetic fields are unable to penetrate the interior because of screening currents induced on the surface, making the superconductor a perfect diamagnet. The screening currents break down under fields exceeding H_c , converting the superconductor to a normal metal, and allowing the flux to enter. The critical current J_c also drives the material back into its normal state, so that the superconducting region is bounded by a critical J - H - T surface. Most engineering developments are concentrated on Nb_3Sn for which T_c is 18.45 °K, H_c is 220 kilogauss at absolute zero, and J_c about 10^5 A/cm². Nb_3Sn is a Type 2 superconductor whose properties are sensitive to defects. A high concentration of dislocations and fine precipitates are needed to maximize J_c . Type 1 superconductors such as Pb and Sn are not as useful but exhibit simpler behavior.

Superconductors show an intermediate state in which normal and superconducting regions co-exist. Boundaries between the two phases often show preferred orientation, even in cubic metals; in lead, the boundaries prefer (100) planes.

Most applications center on the use of superconductors for the generation of high magnetic fields, although another important possibility is in cables for electrical power transmission [13]. Particle physics is presently the most active area of development in superconductor technology since high energy studies require high magnetic fields. Conventional iron-core magnets used in beam handling are being replaced in synchrotrons and bubble chambers. The use of superconductors in the electrical industry is limited to large machines since the cost of refrigeration offset savings elsewhere. Most progress has been made on D.C. machines with superconducting field windings. Other potential uses include transformers, magnetohydrodynamic (MHD) magnets, magnetic bottles for controlled thermonuclear fusion, magnetic ore separators, and high speed trains supported by magnetic levitation. Large quantities of electrical power could be transmitted without loss over long distances using superconducting cables. The power lines would be underground rather than overhead and the loads very large to justify costs.

Many of the applications are marginal economically, so that future development rests partly on improving material parameters. Among the objectives are reduction in the cost of material, improvements in critical values T_c , H_c , and J_c , and reduction of losses in alternating fields.

A great deal of effort has been expended in recent years searching for superconductors with high transition temperatures. Liquid helium (boiling point 4 °K) is generally employed in the study of superconductors, but helium is too expensive for large scale technological applications.

The discovery of $\text{Nb}_3(\text{Al}, \text{Ge})$ and Nb_3Ga has brought superconductivity into the liquid hydrogen range (boiling point 20 °K). There seems to be a misconception, however, that only liquid helium can be used for superconductors having a transition temperature below 20 °K. Hydrogen has been used as a cryogenic fluid down to about 14 °K, well within the superconducting region of several other intermetallic compounds. The boiling point of H_2 drops considerably with pressure, and there is no reason why refrigerators cannot be operated at reduced pressures.

Superconductivity occurs chiefly in metals because insulators, semiconductors and semimetals lack sufficient numbers of conduction electrons. It is a cooperative effect in which electrons are coupled in Cooper pairs, and as such is in competition with other coupled electron effects such as ferromagnetism.

MATTHIAS and co-workers [14] have discovered a number of important superconductors and described several crystal chemistry criteria useful in finding superconductors with high transition temperatures and high critical fields. Perhaps the most useful is the correlation between T_c and n , the average number of valence electrons per metal atom (Fig. 18). Included in n are all electrons outside the closed-shell, d electrons as well as s and p .

From Fig. 18 it can be seen that superconductivity is limited to electron per atom ratios in the range $2 \leq n \leq 8$. There are two important groups of superconductors with different physical mechanisms. Non-transition metal superconductors (Zn, Pb, Sn, Tl, Cd) show isotope effects in which $T_c \sim 1/\sqrt{M}$. This supports the view that electron-phonon-electron interactions give rise to weak attractive forces between electrons, the so-called "Cooper pairs". Bardeen, Cooper and Schrieffer have presented a theory of superconductivity based on weak attractive forces between electrons.

Isotope effects are not so obvious in transition-metal superconductors. Transition metals with odd numbers of electrons show high transition temperatures—except for those with long-range magnetic order. Superconductivity and ferromagnetism appear to be competing cooperative phenomena. The weak attractive force required for superconductivity may arise from s - d - s electron interactions rather than phonon coupling.

Simple crystal structures with short interatomic distances are conducive to high transition temperatures. Among the elements the highest values of T_c are comparable for the three main structure types. The T_c values of lead (FCC), technetium (HCP) and niobium (BCC) are 7, 8, and 9 °K, respectively. Niobium nitride and other interstitial nitrides and carbides having the rock-salt structure also exhibit high transition temperatures.

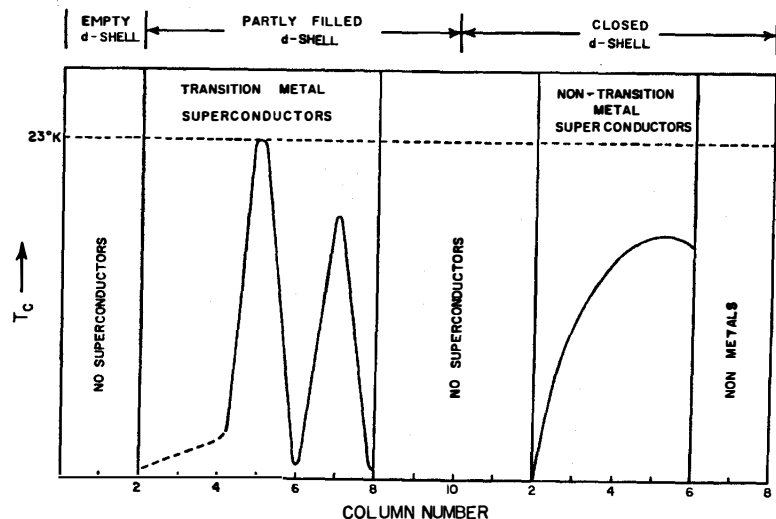


Fig. 18. Superconducting transition temperatures can be correlated with electron/atom ratios. Nb_3Sn is typical of the transition metal semiconductors, while Pb is representative of the non-transition metal group

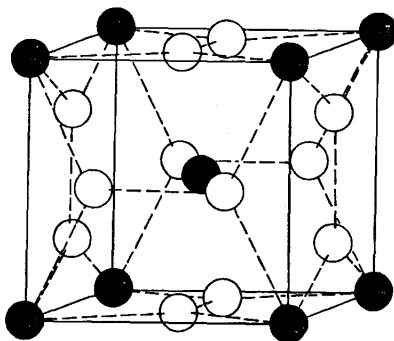


Fig. 19. The crystal structure of β -tungsten. The dark circles represent the Sn positions in Nb_3Sn

The β -W or Cr_3Si structure (Fig. 19) is especially conducive to superconductivity. Nb_3Sn , Nb_3Al , V_3Si , and similar compounds have T_c values between 15 and 20 °K. Twenty degrees Kelvin is very important because this is the boiling point of liquid hydrogen, making feasible the operation of superconductor devices without liquid helium. In explaining the

preference for the β -W structure it is instructive to note the interatomic distances. The shortest Nb-Nb distances in Nb metal, NbN, and Nb_3Sn are 3.8, 3.1, and 2.7 Å, respectively. Thus, T_c appears to increase for shorter interatomic distances. This has led to the speculation that useful new superconductors will be obtained by high-pressure synthesis.

A correlation has been observed between the superconducting critical temperature T_c , and solid solution range appearing in the phase equilibrium diagram of A_3B -type compounds isostructural with β -W [15]. Among the compounds showing incongruent melting, T_c is direct proportional to the solid solution range. At low-temperature, solid solution occurs only for B-rich compositions and never for A-rich compositions. This suggests the fundamental importance of A-chain integrity, an important factor in superconductivity as well. An A-element can substitute for B, but B cannot interrupt the chains by substituting for A.

Another approach to achieving higher transition temperatures and higher critical fields is to enhance electron-phonon interactions. Unfortunately this usually makes the crystal structure unstable, resulting in a phase transition and the loss of superconducting behavior. Reducing the average phonon energy increases the effectiveness of electron-phonon interactions. In Nb_3Sn and other compounds with the β -W structure, phonons associated with $\langle 110 \rangle$ transverse modes possess unusually low energies.

Nb_3Sn , V_3Si and other A15 superconductors are extremely susceptible to tetragonal distortions, causing structural instabilities at low temperatures. Many of the anomalies of high T_c superconductors can be calculated from the strain dependence of T_c , leading to the suggestion that an incipient structural transformation promotes superconductivity. Encouraging a structural instability is one way to raise the superconducting transition temperature [16]. Instabilities occur at the phase boundaries of many metals, especially in transition metal alloys forming σ or α -Mn phases. To promote superconductivity, it will be necessary to induce the instabilities at low temperatures without triggering a structural transformation of appreciable strain.

An example of the importance of structural instability is the recently discovered superconductor $\text{Li}_{0.3}\text{Ti}_{1.0}\text{S}_{1.8}$ [17]. Lithium titanium sulfide is a ternary compound with a high transition temperature of 15 °K and a metastable hexagonal crystal structure. Samples cooled quickly from high temperatures to the liquid helium range display the most desirable characteristics.

Intercalation has not yet resulted in pronounced increases in the superconductivity transition temperature but it has been suggested that more polarizable intercalated molecules may raise T_c . When the conduction electrons are in contact with highly polarizable insulating layers

the electron-pairing interaction (Cooper pairs) is enhanced as each electron responds to the polarization induced in the dielectric by its partner. Interactions such as these between conduction electrons and molecular electrons might produce high superconducting critical temperatures.

Until a few years ago, superconductivity was confined to metals, alloys and intermetallic compounds. There are, however, reports that

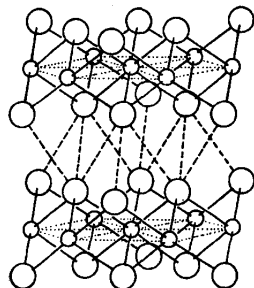


Fig. 20. Portions of two layers of the CdI_2 structure. The small circles represent metal atoms

certain organic solids may show superconductivity. Dimethyltetrathiofulvalenetetracyanoquinodimethane exhibits sporadic superconductivity at 60 °K, three times higher than the best metallic superconductor. It has been suggested that noncrystalline organic solids and polymers may show similar phenomena.

Highly anisotropic superconductors have been produced from intermetallic compounds intercalated with organic molecules. Intercalation of K atoms in graphite raises the electron concentration converting it from a nonsuperconducting semimetal to a superconductor. Crystals of $2\text{TaS}_2 \cdot \text{C}_5\text{H}_5\text{N}$ consist of TaS_2 layers alternating with pyridine molecules giving a periodicity of 12 Å. A chemical bond is formed from the lone pair electrons of nitrogen and the half-filled conduction band of the TaS_2 layers, where $\alpha\text{-TaS}_2$ has the CdI_2 structure (Fig. 20). The intercalation reaction does not proceed in MoS_2 and WS_2 where the conduction band is filled. Superconductivity in such materials is highly directional, being much more readily attained for electrons flowing along the planes than for those flowing perpendicular to the planes. Such experiments require nearly perfect single crystals since dislocations tend to "short out" the electrical anisotropy which ranges from 10:1 to 10^5 :1. Critical temperatures between 1.5° and 4.5°K have been measured in intercalation complexes of TaS_2 and substituted pyridines [18].

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