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CURRENT PROBLEMS IN RESEARCH

Semiconducting Compounds

New semiconductors reveal striking relations between composition and structure.

E. Mooser

In the last two decades electronic devices in the form of photocells, rectifiers, thermistors, transistors, solar cells, radiation detectors, and so on, have rapidly become of outstanding importance not only in research and industry but also in our everyday life. In spite of their widely varying applications and appearances, these devices have something in common: in one form or another they all contain some semiconducting material. As a result of this, a big effort has been made to come to a better understanding of the physics and chemistry of semiconductors. In particular, it was felt that the comparatively small number of semiconducting materials known at the beginning of the last decade was insufficient for our needs, and systematic searches for new semiconducting compounds have been undertaken.

The discovery and subsequent study of a new semiconductor is not only of help to the device engineer, who is constantly on the lookout for the material best suited for his purposes, but is also of fundamental interest because at present the only reliable way to come to an understanding of the influence of chemical composition and crystal structure upon the properties of semiconductors is to investigate series of chemically and structurally similar materials.

As a specific class of solids, semiconductors are perhaps best described in terms of their electrical conductivity, which is somewhere between that of a metal and that of an insulator. More accurately, semiconductors are nearly metallic at high temperatures and nearly insulating at low temperatures. The law — first established experimentally — which governs this strong dependence of the electrical conductivity σ on the temperature T is generally of the form

$$\sigma = A(T)\ e^{-\Delta E/2kT} \qquad (1)$$

where $A(T)$ is a slowly varying function of temperature and ΔE is an energy. Moreover, the conductivity (at least at low temperatures) depends very much on the purity of the semiconducting material and, in the case of a compound, on any deviation from stoichiometric composition. Minute impurity contents (10^{14} to 10^{18} impurity atoms per cubic centimeter) and slight deviations from stoichiometry can increase the conductivity by orders of magnitude.

This behavior was first interpreted in 1931 by Wilson (*1, 2*) in terms of the electron energy spectrum—the band structure—of semiconductors. When an atomic gas condenses to form a solid, the atomic energy levels widen into a series of energy bands. Wilson pointed out that in a semiconductor the number of electrons occupying these bands must be such that all bands up to and including the so-called valence band are completely filled at $T = 0$ and that the next higher band, the conduction band, must be empty and separated from the valence band by a finite energy gap ΔE which is of the order of the thermal energy kT (Fig. 1*a*). In contrast to this, the uppermost occupied energy band in a metal is only partly filled by electrons (Fig. 1*b*). Because at $T = 0$ all energy levels in the valence band are occupied, an electric field applied to a semiconductor cannot increase the translational energy of the electrons: there are no empty states of higher energy available for the electrons to move into. The electrons in the *completely filled* valence band therefore cannot carry an electrical current. However, if some of the electrons of the valence band are excited (thermally or otherwise) across the energy gap into the conduction band, they become free to move throughout the solid. Moreover, the "holes" left behind in the valence band by the excited electrons also contribute to the conduction, because, as can be shown, they behave like free, positive charge carriers.

Statistical mechanics tells us that at temperature T the number n of electrons excited across the gap ΔE, and hence the number p of holes in the valence band, is

$$n = p \propto e^{-\Delta E/2kT} \qquad (2)$$

On the other hand, we know that the electrical conductivity resulting from the presence in a solid of n free electrons and p free holes is given by:

$$\sigma = ne\mu_n + pe\mu_p \qquad (3)$$

where e is the electronic charge and μ_n and μ_p are the mobilities (that is, the velocities in unit electric field) of the electrons and holes, respectively. If we add that both μ_n and μ_p are slowly varying functions of temperature, then we see, by combining Eqs. 2 and 3, that theory does indeed reproduce the experimentally established Eq. 1.

To interpret the influence of impurities upon the conductivity of semiconductors, Wilson (*2*) further showed that impurity atoms introduced substitutionally into the lattice of a semiconductor are responsible for the occurrence in the band structure of additional energy levels. Thus, if the impurity

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The author is a staff member of the Division of Pure Physics of the National Research Council, Ottawa, Canada.

atoms each have one valence electron less than the atoms which they replace, a normally empty energy level occurs at or slightly above the upper edge of the valence band. If the impurity atoms each have one valence electron more than the replaced atoms, a normally occupied level is introduced at or slightly below the lower edge of the conduction band. Electrons can then be excited thermally (or otherwise) from the valence band into the normally empty acceptor level (Fig. 2*a*) or from the normally occupied donor level into the conduction band (Fig. 2*b*). The net result of this is that in a semiconductor containing acceptor or donor impurities, or both, the numbers of both free electrons and free holes differ from the numbers found in the pure material. Equation 3 then informs us that this change in the numbers of charge carriers affects the conductivity, and this is indeed observed experimentally.

Chemical Composition of Semiconductors

While the amount of impurities in a semiconductor can be controlled within certain limits, other parameters, such as the energy gap, are essentially constants of the material, and their values cannot very well be altered. Moreover, the charge carrier mobilities, representative of yet another group of semiconductor parameters, while depending on purity and crystalline perfection, cannot readily be changed in a *controllable* way. It therefore becomes essential to the device engineer to have at his disposal as many different materials as possible so that he can choose the one best suited to a certain application. But beyond the question of technical application, the scientist would like to establish the laws governing the dependence of the properties of semiconductors on their chemical composition, and, therefore, he too has an interest in new semiconducting materials. Moreover, the scientist would like to be able to predict the chemical compositions and crystal structures of any semiconducting phases that might occur in a system of two or more chemical components. The problems involved in making such predictions are beyond the reach of present-day theory, but the first step toward their solution was perhaps made when in 1952 Welker (*3*) predicted and found the semiconducting properties of compounds, such as indium antimonide (InSb), which are formed by the elements of group IIIB of the periodic table with the elements of group VB (see Fig. 3). We assign the general formula $A^{III}X^{V}$ to this family of compounds, thereby indicating that the electropositive partners *A*,*B*, . . . (the cations) are group III elements and the electronegative partners *X* (the anions), group V elements. Analogous formulas are used below to designate other families of compounds. A list of the semiconducting $A^{III}X^{V}$ compounds is given in Table 1, and in Fig. 3 the part of the periodic table which is of interest to us is reproduced.

Table 1. The semiconducting $A^{III}X^{V}$ compounds.

AlP	GaP	InP
AlAs	GaAs	InAs
AlSb	GaSb	InSb

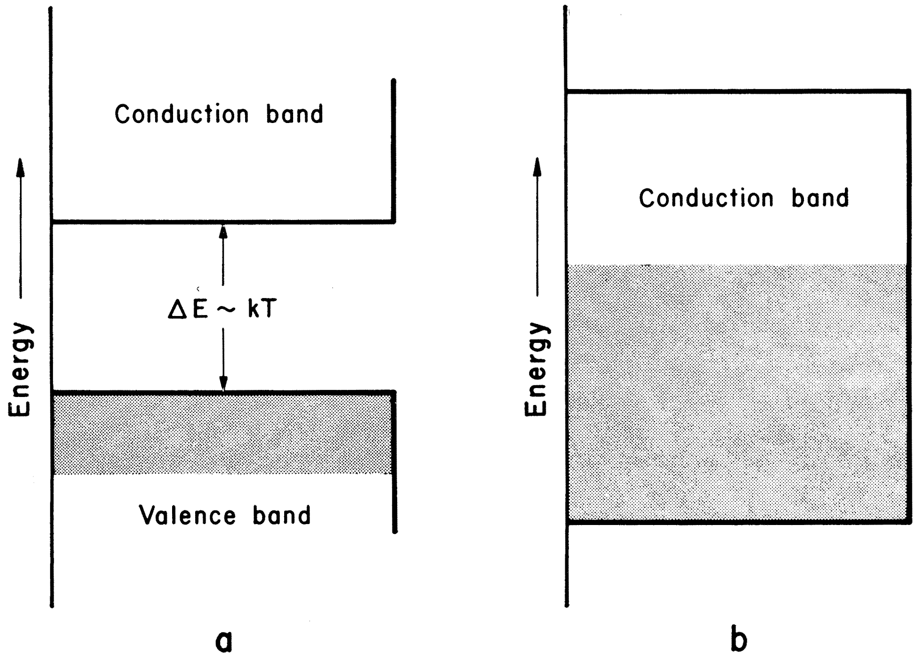

Fig. 1. Schematic band structures of *(a)* semiconductors and *(b)* metals.

Welker's predictions were based on his recognition of the chemical and structural similarities between the $A^{III}X^{V}$ compounds and the group IVB semiconductors silicon, germanium, and grey tin. In both the compounds and the elements the average number of valence electrons per atom is four. Moreover, the zinc blende structure of the $A^{III}X^{V}$ compounds is the same as the diamond structure of the group IVB semiconductors except that in the compounds the lattice sites are occupied by two kinds of atoms (*4*). Since the chemical bonds in compounds always have some ionic character, Welker concluded that they should be stronger than the purely covalent bonds found in silicon, germanium, and grey tin, and on the basis of this qualitative argument he predicted that the compounds aluminum phosphide (AlP), gallium arsenide (GaAs), and indium antimonide (InSb) should have larger energy gaps than the corresponding elements. Moreover, since stronger bonds lead to smaller amplitudes of the thermal vibrations, Welker further predicted that the charge-carrier mobilities in the compounds should also be larger. Both these predictions were subsequently confirmed by experiment.

Unfortunately, these "Welker rules," together with a series of other equally qualitative rules (for a compilation of such rules see, for example, *5*), are at present the only means at our disposal to predict the properties of new semiconductors, and it does not seem likely that this situation will change very much in the near future. If, however, we restrict ourselves to predicting semiconductivity rather than detailed properties, we are in a better position. Thus, Welker's criterion of chemical and structural similarity led to the discovery of the semiconducting properties of the $A^{I}B^{III}X_2^{VI}$ (*6*) and $A^{II}B^{IV}X_2^{V}$ (*7*) compounds such as copper indium telluride ($CuInTe_2$) and zinc germanium arsenide ($ZnGeAs_2$)—compounds which, like the $A^{III}X^{V}$ compounds, have an average of four valence electrons per

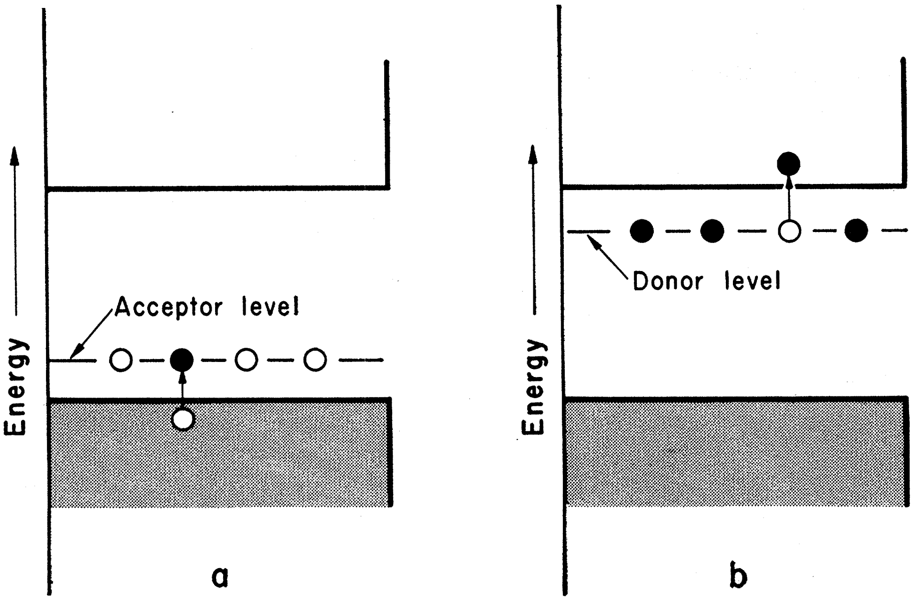

Fig. 2. Band structure of impure semiconductors with *(a)* an acceptor level and *(b)* a donor level.

atom and which have a chalcopyrite structure (see Fig. 6), in which the cations and anions also occupy the lattice sites of the diamond structure. However, there are many semiconductors for which this criterion does not apply, and in order to develop better means for predicting semiconductivity, a more generally applicable criterion was needed. Such a criterion evolved from a survey (*8*) made in 1956 of the chemical bonding in the then known semiconductors.

The bonds in semiconductors are predominantly covalent—that is, they resemble the bond formed in an H_2 molecule. When two hydrogen atoms approach each other their atomic orbitals—that is, the charge clouds associated with the movement of the electrons around the nuclei—begin to overlap until they can no longer be distinguished from one another. The two electrons are then equally shared between the two hydrogen nuclei, and their spins are paired (they point in opposite directions, see Fig. 4). Because covalent bonds result from an overlap of atomic orbitals of neighboring atoms and because most atomic orbitals are not spherically symmetrical, covalent bonds usually have strongly pronounced directional properties. We will see below that this is of considerable importance for the crystal structures of semiconductors. If a covalent bond occurs between two atoms of different kinds, then the electrons are no longer shared equally by them. Instead, the charge cloud formed by the bonding electrons is shifted toward the atom with the higher electronegativity, and the bond is said to have some ionic character. Finally, at large electronegativity differences the electrons are completely centered about the electronegative atom, and the bond is purely ionic.

An atom can form only a limited number of covalent bonds. As soon as the electrons shared by the atom with its neighbors, together with any unshared valence electrons, completely fill the valence subshells—that is, as soon as the valence of the atom is saturated—no further bonds can form. It can be shown that the completion of the valence subshells of the electronegative partners (anions) in a compound leads to a band structure of the type represented in Fig. 1*a*—that is, the compound is a semiconductor. If the electropositive partners (cations) of the compound have the necessary number of valence electrons to saturate the valence of the anions, then the total number N_e of valence electrons per anion must equal the number of states in the valence subshells of the anions. If, in particular, the anions require filled *s* and *p* orbitals—and this is the case in the vast majority of semiconductors—then

$$N_e = 8 \qquad (4)$$

The chemical composition of these semiconductors is, therefore, governed by the same valence rule which holds for many ionic compounds (see, for example, *9*), and one can summarize this discussion of the bonding in semiconductors as follows: Semiconducting compounds are normal valence compounds [exclusive of molecular compounds (*10*)] with predominantly covalent bonding. I should add that in a few semiconductors the total number of valence electrons exceeds eight. However, this electron excess can be compensated by the formation of cation-cation bonds such as are found, for example, in gallium telluride (GaTe) (*11*), where the gallium atoms form pairs. Similarly, a possible deficiency of valence electrons can be compensated by anion-anion bonds. As an example I might mention cadmium antimonide (CdSb) (*12*), in which the anions are linked in pairs. If b_c is the average number of cation-cation bonds formed by each cation and b_a is the average number of anion-anion bonds formed by each anion, then one can rewrite Eq. 4 in the form

$$N_e + b_a - b_c = 8 \qquad (5)$$

thereby taking into account the compensation of any electron excess or deficiency through the formation of bonds between like atoms.

		Group									
		IA	IIA	Transition Elements Groups IIIA — VIIIA	IB	IIB	IIIB	IVB	VB	VIB	VIIB
Period	2	Li				Be	B	C	N	O	F
	3	Na				Mg	Al	Si	P	S	Cl
	4	K	Ca		Cu	Zn	Ga	Ge	As	Se	Br
	5	Rb	Sr		Ag	Cd	In	Sn	Sb	Te	I
	6	Cs	Ba		Au	Hg	Tl	Pb	Bi	Po	At

Fig. 3. The periodic table (transition elements and rare earths excluded).

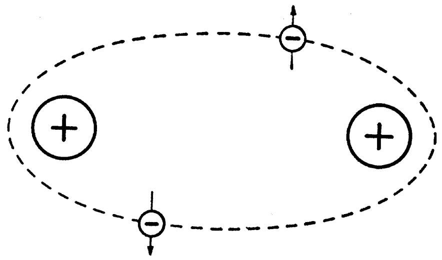

Fig. 4. The covalent bond in the H_2 molecule.

To illustrate this relationship, I have listed (Table 2) the appropriate values of N_e, b_a, and b_c for a series of semiconductors. It is noteworthy that Eq. 5 also holds for elemental semiconductors if in this case all the atoms are considered to be anions. This is a consequence of the filling, in elemental semiconductors, of the *s* and *p* orbitals of *all* atoms.

Through electron sharing an atom can, at the most, acquire as many additional electrons as the number of electrons it already has in its valence shell. In order that the octets on the anions can be completed by the formation of electron pair bonds, the anions, therefore, must have a minimum of four valence electrons. Indeed, all semiconductors for which Eq. 5 holds contain at least one element from groups IVB to VIIB of the periodic table.

Having discussed the rules governing the chemical composition of semiconducting compounds, let us look at a few of these compounds. The simplest among them are those of composition AX whose components lie symmetrically with respect to group IVB. They are the $A^{\mathrm{III}}X^{\mathrm{V}}$, $A^{\mathrm{II}}X^{\mathrm{VI}}$, and $A^{\mathrm{I}}X^{\mathrm{VII}}$ compounds, of which the $A^{\mathrm{I}}X^{\mathrm{VII}}$ ones, such as, for example, rock salt (NaCl), normally show ionic rather than electronic conduction. Owing to the large ionic component in the bonding (the difference between the electronegativities of the constituents is large), the energy gaps are large—larger in fact than the energies necessary to create the lattice defects which give rise to ionic conduction. However, by adding appropriate impurities to these compounds, donor or acceptor levels, or both, can be introduced into their band structure, and then electronic conduction is observed. The tendency of the heavier group IVB atoms tin and lead to retain their *s* electrons and thus to act as bivalent cations gives rise to the lead sulfide (PbS) family of semiconductors. By substituting pairs of *unequal* cations for every two cations of the AX compounds mentioned above, one arrives at a series of ternary compounds which all have semiconducting properties, provided only that Eq. 5 is not violated by the substitution. Best known among them are the $A^{\mathrm{II}}B^{\mathrm{IV}}X_2^{\mathrm{V}}$ (*7*), $A^{\mathrm{I}}B^{\mathrm{III}}X_2^{\mathrm{VI}}$ (*6*), and $A^{\mathrm{I}}B^{\mathrm{V}}X_2^{\mathrm{VI}}$ (*13*) compounds like zinc germanium arsenide, copper indium telluride, and silver bismuth sulfide ($AgBiS_2$), which are direct derivatives of indium arsenide (InAs), cadmium telluride (CdTe), and lead sulfide, respectively.

Leaving the AX compounds and their ternary derivatives, I next mention the cation-rich compounds of composition A_2X. Perhaps the best known among them is magnesium stannide (Mg_2Sn) (*14*), in which the two magnesium atoms provide the four electrons necessary to complete the octet on tin. If in magnesium stannide we substitute a group VIB atom for tin and, to satisfy Eq. 5, a group IA atom for magnesium, we arrive at the $A_2^{\mathrm{I}}X^{\mathrm{VI}}$ compounds (Li_2Se and so on), whose crystal structure is the same as that of magnesium stannide. Little is known about their properties, but because of the large electronegativity differences between the components, one would expect them to be ionic conductors. There are some ternary derivatives of the A_2X compounds which also have the structure of magnesium stannide, but so far only lithium magnesium antimonide (LiMgSb) and lithium magnesium bismuthide (LiMgBi) have been shown to be semiconductors (*15*). A number of $A_3^{\mathrm{I}}X^{\mathrm{V}}$ compounds, such as lithium bismuthide (Li_3Bi) (*16*), and other alkali metal compounds are known to be semiconducting, and so is the ternary derivative lithium magnesium stannide (Li_2MgSn) (*17*), which has the same structure. To end the list of cation-rich semiconductors I mention the $A_3^{\mathrm{II}}X_2^{\mathrm{V}}$ compounds such as magnesium antimonide (Mg_3Sb_2), whose semiconducting properties have been studied in various laboratories (see, for example, *18*).

Table 2. Appropriate values of N_e, b_a, and b_c for a series of semiconductors.

Semiconductor	N_e	b_a	b_c	$N_e + b_a - b_c$
InSb	3 + 5			8
PbS	2 + 6			8
In_2Te_3	[(2 × 3) + (3 × 6)]/3			8
CdSb	2 + 5	1		8
GaTe	3 + 6		1	8
Ge	4	4		8
Se	6	2		8

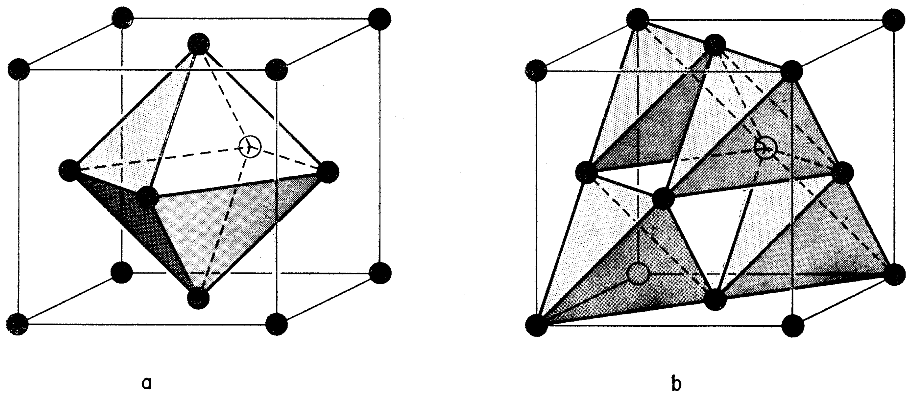

Fig. 5. (*a*) The octahedral and (*b*) the tetrahedral holes in the close-packed cubic structure.

Considering anion-rich compounds next, we note that most of those of composition AX_2 are predominantly ionic. Nevertheless, there are some semiconductors of this composition, such as tin disulfide (SnS_2). Of the AX_3 compounds, the group VB triiodides (BiI_3 and so on) are known to be semiconducting. Most anion-rich semiconductors are, however, found at lower anion-to-cation ratios. Thus, semiconducting properties have been found in a series of $A_2^{\mathrm{III}}X_3^{\mathrm{VI}}$ (*19*) (In_2Te_3 and so on) and $A_2^{\mathrm{V}}X_3^{\mathrm{VI}}$ compounds. Among the latter, bismuth telluride (Bi_2Te_3) (*20*) has become rather important in the last few years because of its thermoelectric properties. Of the anion-rich ternaries, the $A^{\mathrm{II}}B_2^{\mathrm{III}}X_4^{\mathrm{VI}}$ (*21*) compounds ($HgIn_2Te_4$ and so on) are known to be semiconductors.

The above list of semiconducting compounds is far from complete. Nevertheless it gives a good indication of the great variety of semiconducting materials known at present, and it also serves to illustrate the rules governing the chemical composition of semiconductors. However, no mention has been made of compounds containing transition elements (titanium, iron, cobalt and so on), in spite of the fact that many of them show semiconducting properties. The reasons for this omission are that (i) we do not usually have an a priori knowledge of the valence of the transition elements and, therefore, the rules mentioned earlier cannot be applied to predict semiconductivity, and (ii) it is usually very difficult to produce transition element compounds in such a form that their *intrinsic* electrical properties can be studied accurately. Here, then, is a vast field of research open to both the theoretician and the experimentalist.

Crystal Structures of Semiconductors

Detailed data on the electrical properties are at present available only for the AX compounds. However, the crystal structures of all the semiconductors listed in the preceding section have been determined, and it is, therefore, possible to develop a systematics of semiconducting structures (*5, 17, 22*).

The bonds in semiconductors are predominantly covalent, and it was mentioned above that covalent bonds have pronounced directional properties. We therefore expect the arrangement of the neighbors of each atom in a semiconductor—in other words, the coordination of the atoms—to be typical of directed bonds. In fact, we expect tetrahedral and octahedral coordinations to prevail because they arise from the formation of tetrahedral sp^3 bonds and octahedral p bonds, respectively, and we know that it is mostly the s and p electrons which are involved in the bonding in semiconductors. Looking for three-dimensional arrays of equal atoms which are particularly adaptable for these coordination configurations, we find that close-packed structures contain one octahedral and two tetrahedral holes per close-packed site. Figure 5*a* shows the one octahedral hole lying completely inside the unit cell of the cubic close-packed (face-centered cubic) structure. Only the centers of the close-packed spheres are marked. In Figure 5*b* four of a total of eight tetrahedral holes lying within the unit cell are shown. It may be readily seen from these figures that if the anions of a compound form a close-packed array and if the cations occupy some or all of the tetrahedral or octahedral holes, or both, of the anion sublattice, then tetrahedral or octahedral coordination, or both, results. This filling by cations of the holes in a close-packed array of anions is the "Aufbau principle" of most semiconducting structures. Thus, Fig. 6 shows how filling by cations of half of the tetrahedral holes in a cubic close-packed array of anions leads to the zinc blende (ZnS) structure of many $A^{III}X^{V}$ (InSb), $A^{II}X^{IV}$ (ZnS) and $A^{I}X^{VII}$ (AgI) compounds and to the chalcopyrite structure of the ternaries of composition $A^{I}B^{III}X_2^{VI}$ ($CuInTe_2$) and $A^{II}B^{IV}X_2^{V}$ ($ZnGeAs_2$). Filling of all tetrahedral holes results in the fluorite structures of magnesium stannide and its derivative lithium magnesium antimonide. The rock-salt structure of many $A^{I}X^{VII}$, $A^{II}X^{VI}$, $A^{IV}X^{VI}$, and $A^{I}B^{V}X_2^{VI}$ compounds (NaCl, CdO, PbS, $AgBiS_2$) is obtained if the cations are filled into the octahedral holes. As indicated in Fig. 6, the structure of lithium bismuthide (Li_3Bi) (the same is true of Li_2MgSn) is a superposition of the fluorite and the rock-salt structures, both the octahedral and the tetrahedral holes being occupied. Partial filling of the cation sites of the zinc blende struc-

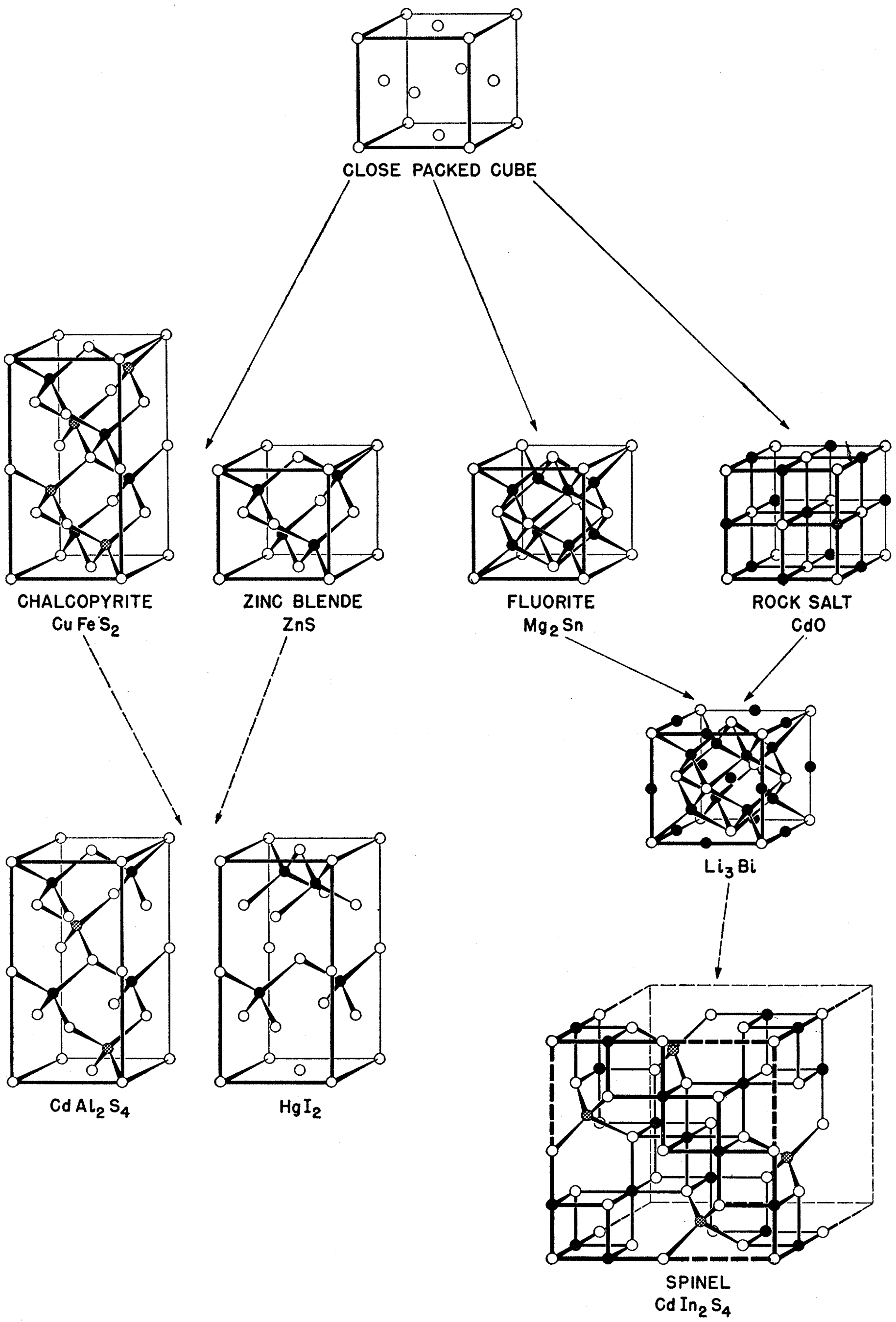

Fig. 6. Derivation of some semiconducting structures from the close-packed cubic structure.

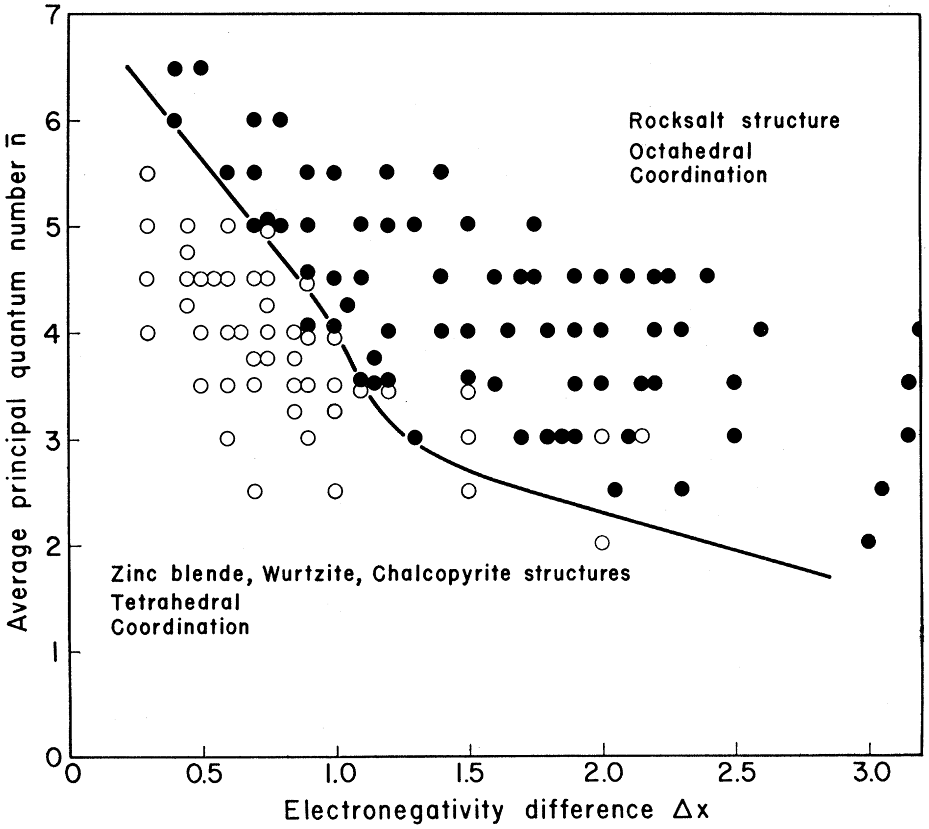

Fig. 7. *AX* structures with cubic close-packed anion substructures and tetrahedral and octahedral coordination.

ture gives rise to the structure of the ternaries of composition $A^{II}B_2^{III}X_4^{VI}$ ($CdAl_2S_4$) as well as to the structures of indium telluride (In_2Te_3) and mercury iodide (HgI_2). Figure 6 also shows that the spinel structure, which is found in many semi-conductors containing transition elements, can be considered as a lithium bismuthide structure in which some of the cation sites remain unoccupied. In the wurtzite (ZnS), nickel arsenide (NiAs), cadmium iodide (CdI_2), and bismuth triiodide phases, as well as in magnesium antimonide, the anions form a hexagonal rather than a cubic close packing, and again the cations are located in the tetrahedral or octahedral holes, or both, of the anion sublattice. More complicated anion close packings are observed, for example, in silicon carbide (SiC) and bismuth telluride (Bi_2Te_3).

At this point a series of questions come to mind: At what chemical compositions do structures with close-packed anion arrays form? When do the cations prefer to fill the tetrahedral holes, when the octahedral holes? How are the cations distributed among the available holes if there are fewer cations than holes? Is there a relationship between the chemical composition and the particular type of close packing of the anions? While we do not at present know all the answers, some progress has been made towards finding them. Thus we know (*23*), for instance, that nondirectionally bonded phases prefer highly symmetrical and densely packed structures which lead to the best possible filling of space. Accordingly, the numbers of neighbors of each atom—that is, the coordination numbers—are higher in these phases than in the rather loosely packed directionally bonded solids. We also know (*24*) that covalent bonds between light atoms have the most pronounced directional properties and that these properties gradually diminish as the bonded atoms become heavier. If in a series of chemically similar and covalently bonded solids we go from the light to the heavy representatives, we therefore expect to meet crystal structures whose packing gradually becomes denser and leads to higher coordination numbers. The group IVB elements and their structures may serve as an illustration. Solid carbon is found in two modifications, graphite and diamond, in which the coordination numbers are 3 and 4, respectively. The intermediate elements silicon, germanium, and tin also crystallize in the diamond structure, but in tin we already meet a second metallic modification (white tin) with a coordination number of 6. In lead this trend towards nondirectionally bonded metallic structures results in a cubic close packing with a coordination number of 12.

The same trend is observed in compounds, and it was found (*5, 22*) that the average principal quantum number $\bar{n}$ of the valence shells of the constituents is a convenient measure for the directional properties of the bonds in compounds (*25*). Strongly pronounced directional properties only occur at small values of $\bar{n}$. However, in compounds we must take into account also the ionicity of the bonds. Ionic bonds are nondirectional, and taking the electronegativity difference Δx as a measure for the bond ionicity, we expect densely packed structures and high coordination numbers whenever Δx is large. As an example, we consider compounds of composition *AX*. Plotting them in an $\bar{n}$ versus Δx diagram (Fig. 7), we find that the zinc blende and wurtzite phases, in which the cations occupy tetrahedral holes, fall within the lower left part of the diagram, where $\bar{n}$ or Δx, or both, are small. At large values of $\bar{n}$ or Δx, or both, on the other hand, we find the compounds crystallizing in the denser rock-salt structure (coordination number 6), in which the cations sit in the octahedral holes. Also plotted in Fig. 7 are the chalcopyrite phases of composition $A^{I}B^{III}X_2^{VI}$ and $A^{II}B^{IV}X_2^{V}$. They, too, are directionally bonded and therefore, like the zinc blende and wurtzite compounds, they lie on the lower left of Fig. 7. Here, then, we find a partial answer to the question of when the cations occupy the tetrahedral and when the octahedral holes. Moreover, since the majority of *AX* compounds crystallize in either the zinc blende, wurtzite, or rock-salt structure, Fig. 7 facilitates the prediction of the crystal structures of new phases.

The situation is somewhat more involved in compounds with anion-to-cation ratios differing from 1. Nevertheless, the directionally bonded phases still separate from the nondirectionally bonded ones on an $\bar{n}$ versus Δx plot, and valuable information on the systematics of semiconducting structures can be gained from such plots (see *22*).

Conclusions

Rather than describe the detailed properties of a few semiconducting compounds and the theoretical efforts that are being made to interpret them, I have tried here to put the emphasis on those basic properties that are common to all semiconductors and that distinguish them from other solids. It is interesting as well as surprising to see how the many and various semiconducting compounds are all governed by the same simple chemical and structural rules. These rules present a challenge to the theoretician, who has yet to interpret them in a rigorous way. They present a challenge also to the experimentalist because they introduce him to large families of new and unexplored semiconducting materials. And the challenge is all the greater since it is to be expected that, as our knowledge of semiconductors and their properties increases, the chemical and structural rules will be reflected in at present largely unknown but much-sought-for relationships between the chemical composition and structure of semiconductors on the one hand and parameters such as energy gap and charge-carrier mobility on the other.

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Doomsday: Friday, 13 November, A.D. 2026

At this date human population will approach infinity if it grows as it has grown in the last two millenia.

Heinz von Foerster, Patricia M. Mora, Lawrence W. Amiot

Among the many different aspects which may be of interest in the study of biological populations (*1*) is the one in which attempts are made to estimate the past and the future of such a population in terms of the number of its elements, if the behavior of this population is observable over a reasonable period of time.

All such attempts make use of two fundamental facts concerning an individual element of a closed biological population—namely, (i) that each element comes into existence by a sexual or asexual process performed by another element of this population ("birth"), and (ii) that after a finite time each element will cease to be a distinguishable member of this population and has to be excluded from the population count ("death").

Under conditions which come close to being paradise—that is, no environmental hazards, unlimited food supply, and no detrimental interaction between elements—the fate of a biological population as a whole is completely determined at all times by reference to the two fundamental properties of an individual element: its fertility and its mortality. Assume, for simplicity, a fictitious population in which all elements behave identically (equivivant population, *2*) displaying a fertility of γ_0 offspring per element per unit time and having a mortality $\theta_0 = 1/t_m$, derived from the life span for an individual element of t_m units of time. Clearly, the rate of change of N, the number of elements in the population, is given by

$$\frac{dN}{dt} = \gamma_0 N - \theta_0 N = a_0 N \qquad (1)$$

where $a_0 = \gamma_0 - \theta_0$ may be called the productivity of the individual element. Depending upon whether $a_0 \gtreqless 0$, integration of Eq. 1 gives the well-known exponential growth or decay of such a population with a time constant of $1/a_0$.

In reality, alas, the situation is not that simple, inasmuch as the two parameters describing fertility and mortality may vary from element to element and, moreover, fertility may have different values, depending on the age of a particular element.

To derive these distribution functions from observations of the behavior of a population as a whole involves the use of statistical machinery of considerable sophistication (*3*, *4*).

However, so long as the elements live in our hypothetical paradise, it is in principle possible, by straightforward mathematical methods, to extract the desired distribution functions, and the fate of the population as a whole, with all its ups and downs, is again determined by properties exclusively attributable to individual elements. If one foregoes the opportunity to describe the behavior of a population in all its temporal details and is satisfied

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The authors are members of the staff of the department of electrical engineering, University of Illinois, Urbana.