6 December 1963, Volume 142, Number 3597 SCIENCE

# Intermetallic Compounds

## These compounds are formed by the interaction of two or more metallic or semimetallic elements.

Wayne W. Scanlon

The search for materials to fill the special needs of our advancing technology has led the metallurgist, chemist, and solid state physicist to look more intensively at intermetallic compounds, many of which have properties totally unlike those of the component elements.

Originally the term intermetallic compound described a group of compounds formed between metallic atoms. This definition is no longer completely valid since a number of the elements which were once called metals because of their metallic luster are not true metals if judged on the basis of electron-energy band structure, which for metals consists of a partially filled valence band or a substantial overlap of higher energy band with a filled valence band.

However, compounds of these nonmetals are still called intermetallic compounds. The elements in question are bismuth, antimony, arsenic, germanium, silicon, selenium, and tellurium. The elements of column V in the periodic table, Bi, Sb, and As, are now known to be semimetals since their filled valence band overlaps only slightly the next permitted band of electron energies. For completeness, phosphorus might be included in this group. The elements Ge and Si in column IV and Se and Te in column VI are semiconductors since there is an energy gap between the filled valence band and the next higher band of energies. For reasons of completeness sulfur is included in this group because of the similarity of its chemical compounds and those of Se and Te.

The term compound means somewhat different things to the chemist, physicist and metallurgist. Here compound is used in the broadest sense of the word, and all cases of atomic linkage, whether ionic, homopolar, or metallic may be considered fundamentally chemical in character. With this definition there is an almost continuous range of chemical combinations which differ in degree from the more rigorous electrovalent and homopolar compounds to the more loosely determined proportions found with the interatomic linkage in metals.

### Binary Intermetallic Compounds

Intermetallic compounds can be formed of two elements obeying customary valence rules though there are frequent departures from these rules. Even in the case of elements which do form compounds of normal valence, abnormal compounds are likely to occur. For example in the sodium and tin compounds, stable structures for $Na_2Sn$, $Na_2Sn_3$, NaSn, and $NaSn_2$ do occur. Another remarkable series is formed from mercury and sodium. Here no less than seven compounds are formed: $Hg_4Na$, $Hg_2Na$, $Hg_{13}Na_{12}$, HgNa, $Hg_2Na_3$, $Hg_2Na_5$, and $HgNa_3$. Here clearly the compositions of the compounds cannot be predicted from simple rules of valency.

There are some rules which govern the formation of intermetallic compounds. In an assembly of atoms of two kinds, there are a number of factors which contribute to stable structure. These include electronic charge—the sharing or transferring of valence electrons between atoms—and some purely geometrical considerations dealing with relative sizes of atoms or ions.

### Geometrical Considerations

There are two important size factors which result in two general types of solid compounds. One results in interstitial compounds and the other in substitutional compounds.

Interstitial compounds may be formed if there is a difference in atom size large enough to allow the smaller atom or ion to fit into the interstices of the lattice of the larger atom; examples of this type of compound are carbon in iron or boron and nitrogen in some transition elements.

Substitutional compounds are far more numerous. They are generally metallic in their electrical properties. In the crystal lattice of these compounds one atom may substitute for the other in forming a common lattice. In this type of compound similarity in atom size is to be desired since the interactions of this type, become very restricted when atom diameters differ by more than 15 percent. There is a tendency for a given atom in these substitutional compositions to surround itself with more neighbors of the opposite kind than would be expected from a purely random distribution. This short-range ordering is favored by increasing difference in electronegativity of the two atom species. Short-range order is found in CuAu and in $Cu_3Au$ at high temperatures.

---

The author is senior scientist, applied physics department, Naval Ordnance Laboratory, Silver Spring, Md. This article is based on a lecture given before the New England regional conference of the Metallurgical Society of the American Institute of Mining, Metallurgy, and Petroleum Engineers in Boston, Massachusetts, 16 May 1963.

On the other hand there is a long range type of ordering which occurs in lattices where atom sizes become so unequal that the crystal is strained. In such cases, a superlattice may form to relieve the strain. Superlattices occur in materials like $Cu_3Au$, CuZn, and AgCd at low temperatures. In general a superlattice tends to form as the difference in the electronegativity between the atoms in the crystal increases, giving rise to a stable structure with a more or less simple chemical formula.

### Electrical Considerations

A dominant factor contributing to the formation of intermetallic compounds has an electrical origin, and concerns the nature of the bond between the atoms in the crystal. These bonds are of three specific types; ionic, covalent, or metallic. However, in any real compound, the bonds may have an almost continuous range of combinations of these three types.

### Metallic Bonding

Metallic bonding arises from the presence of an electron gas, and is accomplished by the attraction of the positive ions for the shared valency electrons. This type of bonding imposes the least restrictions upon the proportions of the constituent elements in the compound. Hence the solid phase may exist with quite wide deviations from stoichiometry. To qualify as a compound, however, this range must be somewhat restricted so that the atoms exist in some simple numerical proportions in the crystal. Atoms of the same kind occupy similar lattice positions.

### Hume-Rothery Ratios

In many intermetallic compounds the stable structure is determined primarily by electron concentrations in relation to atom concentrations. Other factors being favorable, solid phases appear to be associated with certain ratios of valence electrons to atoms. These ratios were first pointed out by Hume-Rothery and were given his name (*1*). Some of the ratios in many of these compounds are 3 : 2, 7 : 4, 21 : 13. A few examples of these intermetallic compounds include CuZn, $Cu_3Al$, and $Cu_5Sn$ which have a ratio of three valency electrons to two atoms; $Ag_5Cd_8$, $Cu_9Al_4$, and $Co_5Zn_{21}$ which have electron-atom ratios of 21 : 13; while the ratio of 7 : 4 occurs in $CuZn_3$, $Au_3Sn$, and $FeZn_7$. Those compounds in which electron concentration is the essential factor determining the structure are called electron compounds. The tendency of an electron compound to develop order increases with increasing difference in electronegativity of the atoms. Accompanying this trend is a tendency to form polar compounds.

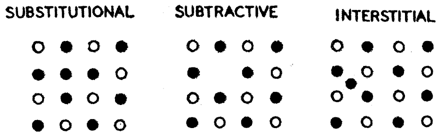

Fig. 1. Point defects in a diatomic crystal.

In a similar fashion, electronic compounds composed of atoms which have tendencies to form covalent bonds tend to blend into covalent crystals with increasing covalent bond strength. Hence there is no sharp boundary between electron compounds and polar and covalent compounds. It becomes apparent that the actual state of affairs in many compounds is confusing, since many different types of interatomic cohesion may be superimposed and may be modified further by atom size ratios.

### Electrical Conductivity

The electrical conductivity of intermetallic compounds depends, among other things, upon the nature of the interatomic forces. When these forces result from the interactions between an electron gas and a positive-ion lattice, as in a metal, the conductivity is high. With increasing tendency to ionic or covalent bonding forces, the valence electrons become more restricted in their freedom and the number of conduction electrons and conductivity decreases—in theory to zero at absolute zero of temperature. Intermetallic compounds having restricted valence electrons are called semimetals and semiconductors, or insulators, depending upon the interplay of the various factors resulting in a stable structure. Those intermetallic compounds which have relatively large covalent or ionic bonds, are the ones having semiconducting properties. In considering these, it must be realized, that in nature an almost continuous range of electrical properties in intermetallic compounds is possible, depending upon the degree of chemical combinations occurring from electrovalent and homopolar compounds to the interatomic linkage of metals and alloys.

The electrical properties of ionic and covalent intermetallic compounds depend to a large degree upon the kind and concentration of defects in the crystal lattice. Defects may be introduced accidentally in the growth of a crystal or they may be always present as a natural result of equilibrium conditions at a given temperature. These defects may result in low-lying energy levels in the forbidden energy gaps of the semiconductors and may contribute or accept charge carriers from the conduction bands. In this discussion only the properties of crystals free from impurity shall be considered. Hence the free electrons or holes in the semiconductors discussed will be due to certain point defects in the crystal structure.

### Covalent and Ionic Bonding

In intermetallic compounds with predominantly covalent or homopolar bonding between atoms, fairly exacting conditions are imposed on the atoms. Not only must certain valence considerations be met but the orientation of the bonds is fixed. As a result crystal composition tends to conform closely to the chemical composition given by the formula, permitting few defects which might lead to low-lying energy levels. Examples of strongly covalent intermetallic compounds are the compounds of group III-V. Within the present limits of preparation these materials seem to conform to the exact stoichiometric proportions of the atoms. At the present time InSb has been prepared with free-electron or hole concentrations as low as $10^{13}$ per $cm^3$ (*2*). This low concentration of free charges is comparable to the best Ge or Si prepared so far. Thus if the composition of this intermetallic compound departs from the exact formula, it must be less than one atom in about $10^9$.

In ionic compounds, on the other hand, while valence considerations are still important, the directions of the bonds between atoms are completely

|  | EXCESS IONS | CONDUCTIVITY | EXAMPLE |
|---|---|---|---|
| (a) | CATION | n-TYPE | NaCl with Cl vacancies (F centers) |
| (b) | ANION | p-TYPE | FeO, CuI |
| (c) | EITHER CATION OR ANION | n or p-TYPE RESPECTIVELY | PbS, TiO, etc. |

Fig. 2. Types of subtractive crystals.

unspecified. The orientation giving the greatest possible number of opposite charges around a given ion consistent with the effects of ion-size gives the stable structure. This less demanding structure permits the incorporation of various point defects in the crysal contributing electrons or holes to the conduction bands and resulting in characteristic electrical properties. These defects may be extra atoms of one or both species in the lattice, interstitial atoms, or vacancies in one of the sublattices. Electrical neutrality is preserved by the presence of the extra electrons or holes in the crystal.

### Limits of Deviation from Stoichiometry

In theory, all crystalline substances should have vacant atom sites or interstitial atoms at finite temperatures. In some crystals, as apparently is the case for the III-V compounds, these concentrations are below present limits of detection. Generally the defects are much less than 1 percent since more than this tends to distort and break up the crystal structure. Exceptional cases are known where several percent excess or deficiency of one atom species can be incorporated in the crystal. Even a few hundredths of a percent of defects that act as donor or acceptor levels in the band structure of a semiconductor may result in electron or hole concentrations of the order of $10^{18}$ or $10^{19}/\mathrm{cm}^3$. Hence these slight departures from the exact chemical proportions are generally very important in intermetallic semiconductor compounds.

### Defects in Crystals

There are three principal types of defects which may be incorporated in a diatomic crystal, so that it exists with an excess of one or the other atom species in thermal equilibrium with the crystal. These are illustrated in Fig. 1. In the crystal with a substitutional defect, the excess atoms of one species occupy lattice sites normally occupied by atoms of the other species. This requires unusual valency conditions in a semiconductor so that this defect is rare. In the subtractive crystal, which is most common, the excess of one atom species is accompanied by vacancies in the other atom sublattice. The crystal with the interstitial defect has atoms sufficiently different in size so that the smaller atom can fit into the interstices without serious strain. This type of defect is therefore not found in many crystals.

In any real crystal, all three types of lattice defects could be present simultaneously in theory; but in practice, one type generally dominates. It is possible to distinguish the dominant defect type on the basis of electrical conductivity tests or density tests. Crystals with substitutional defects will conduct by electrons when there is an excess of the anion or conduct by holes with an excess of the cation. Subtractive and interstitial defect crystals are just the opposite, being electron conducting or *n*-type when the excess atom is the cation and hole conductivity, or *p*-type when the excess atom is the anion.

Subtractive and interstitial defect crystals may often be distinguished on the basis of careful density measurements. Subtractive defect crystals have a smaller measured density than the value determined from x-ray lattice measurements while the interstitial defect crystal is more dense than the x-ray value indicates.

Substitutional defect crystals are likely to be intermetallic compounds in which ion repulsion is weak. Furthermore, a difference of atom valency of unity is desired. Few compounds meet these requirements. The best example is $Bi_2Te_3$. Excess Te atoms may reside on sites normally occupied by Bi, resulting in *n*-type conductivity. Excess Bi in sites normally occupied by Te results in *p*-type conductivity.

The largest number of defect crystals are of the subtractive type and they may be further subdivided into three general classes, illustrated in Fig. 2. The classical example of the first class of crystals having the subtractive type defect is an alkali halide. In NaCl, for example, excess Na is in normally Na lattice positions while a corresponding number of Cl sites are vacant. Charge neutrality in the crystal is preserved by electrons trapped in the Cl sites (*F*-centers). These crystals are *n*-type.

The second class of subtractive defect crystals is one which tends to have an anion excess so that vacancies occur in the cation sublattice. Such crystals are *p*-type. Examples are FeO and CaI. The third class of subtractive defect crystals may have vacancies in either sublattice and the semiconductor is *n*-type or *p*-type depending upon whether there is an excess of cations or anions in the crystal. Examples are PbS, TiO, and many other crystals which have an appreciable ionic bond.

A schematic two-dimensional illustration of the ions in a typical subtractive defect crystal, PbS, is shown in Fig. 3. Excess Pb could be incorporated in the crystal by having either S-ion vacancies or interstitial Pb accompanied by S-ion vacancies as shown. Electrical neutrality in the crystal

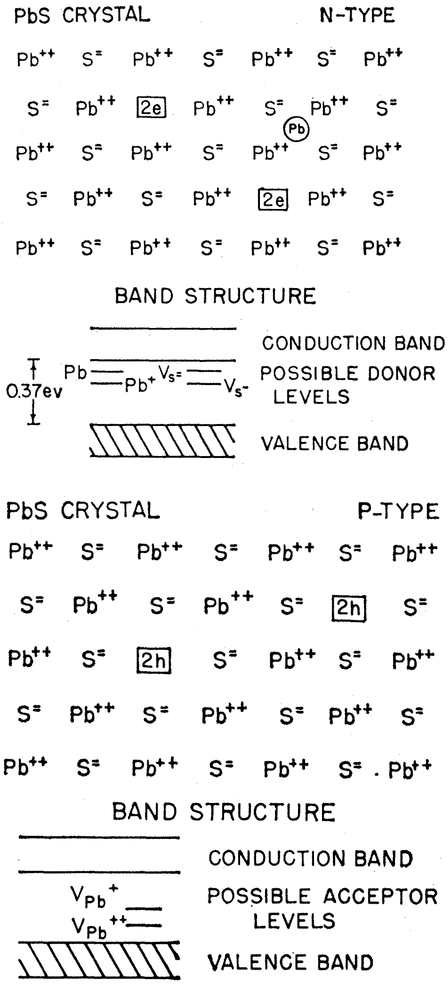

Fig. 3. Vacancies and interstitial atoms in a typical subtractive crystal and their predicted energy levels in the forbidden energy band of the semiconductor. The numerical values were found experimentally.

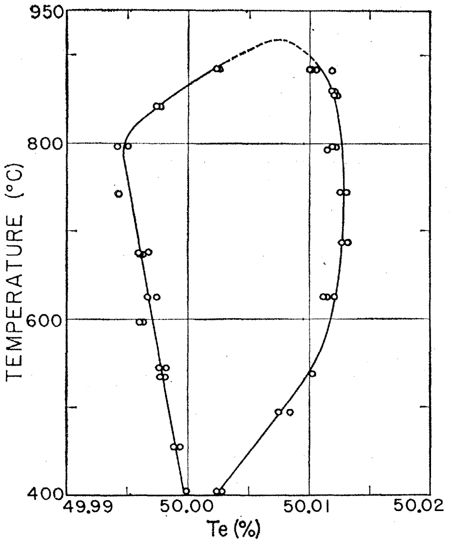

Fig. 4. Composition stability limits for PbTe crystals.

tal is preserved by two electrons associated with each vacancy in the sulfur sublattice at absolute zero. Sulfur excess can be accommodated in this crystal only by vacancies in the Pb sublattice since the S atom is too large to fit in the interstitial position. Electrical neutrality is preserved in this case by having two positive charges, or holes, associated with each Pb vacancy. The corresponding energy levels predicted for the vacancies are illustrated in Fig. 3.

## Equilibrium Conditions for Defects in Crystals

In principle, all crystals of compounds should incorporate concentrations of defects at temperatures above absolute zero. These defects constitute departures from the exact stoichiometric proportions of the elements. The equilibrium concentrations of the defects depend upon the temperature, the nature of the bonds between atoms, the composition of the surrounding liquid or solid phases, or the type and concentrations of impurity atoms in the crystal.

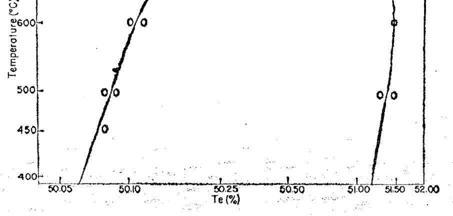

Fig. 5. Solidus line for tin telluride.

There are two aspects of the nonstoichiometry which are of interest in semiconducting intermetallic compounds. One is the temperature dependence of the maximum departure from the ideal composition. The other is the composition of the solid within the limits of maximum departure from stoichiometric composition.

The first of these may be represented by a detailed phase diagram for the composition of the solid in equilibrium with the liquid. The usual scale in phase diagrams is such that the solid phase is a straight line at the composition corresponding to the ideal formula. In practice, however, this line has a width indicating the maximum limit of deviation from the idealized formula. Ordinary chemical methods are generally insensitive to the small departures from stoichiometry which are of interest to the semiconductor physicist.

The Hall effect (*3*) provides a powerful means for studying these small departures in composition and a number of semiconductor materials have been investigated for nonstoichiometry. Among these are the semiconductors PbS, PbSe, PbTe and SnTe. Examples of the high resolution required in these studies are shown in Fig. 4 for PbTe and Fig. 5 for SnTe. Here it can be noted that the departures from the ideal formula are of the order of a few hundredths of a percent. In the case of PbTe, the maximum melting point for the solid phase lies in the excess Te composition. Hence the first solid to form from a stoichiometric melt is *p*-type. Also of interest is the retrograde regions of solubility of the excess atoms in both the *n*-type and *p*-type solid below temperatures of about 700°C.

In the case of SnTe the entire solid phase appears in the region where Te is in excess. Also, as in the case for PbTe, the composition appears to approach the stoichiometric proportions as the equilibrium temperature approaches absolute zero.

Within the solid-phase region the equilibrium concentration of defects in the crystal depends upon the temperature and composition of the surrounding phase. Generally the solid is considered in equilibrium with its vapor. One can write the reaction equations for each of the processes which can occur and the corresponding mass action equation.

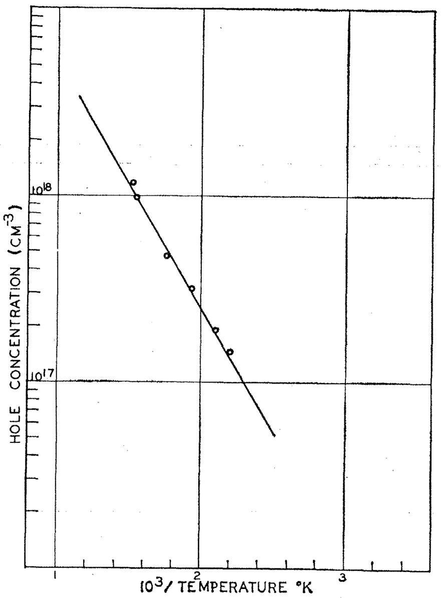

Fig. 6. Precipitation of Te in PbTe crystals.

These equations along with the requirement for electrical neutrality and the Schottky constant for the vacancies enable one to derive an analytical expression for the equilibrium of defects in the solid as a function of partial pressure of the vapor (*4*).

The relationship between partial pressure of the vapor and the crystal composition, and hence its electrical properties, has also been found experimentally for a number of intermetallic compounds such as PbS, PbSe, and CdS. These relationships provide a means for controlling the electrical properties of semiconductors. The desired equilibrium compositions can be established at an elevated temperature where diffusion is fairly rapid and the solid can then be quenched to room temperature to set the composition. Since diffusion is extremely slow near room temperature these crystals, though not now in equilibrium, remain fixed in their composition at the lower temperature.

The crystal composition can be controlled in another way besides vapor-solid equilibrium conditions described previously. In some solids the regions of retrograde solubility can be utilized to alter crystal composition. In PbTe (Fig. 4) both *n*-type and *p*-type crystals which have the saturation amounts of excess atoms at temperatures below 700°C will become supersaturated when reduced further in temperature.

The excess material of one atomic type can be made to diffuse to dislocations where it precipitates. The concentration of vacancies in the other atomic sublattice is therefore reduced along with a reduction in concentration of conduction electrons or holes in the semiconductor. The equilibrium concentration of holes in PbTe crystals as a function of precipitation temperature is shown in Fig. 6 (*5*). This method could in principle be pursued to very low charge carrier concentrations but is limited in practice by the increasingly long diffusion times required to reach equilibrium at lower temperatures.

## Summary

Thus, formation of intermetallic compounds must satisfy certain geometrical and electrical considerations, including favorable ion-size ratios, electron to atom ratios and electronegativity ratios. There is no sharp boundary between compounds which have metallic characteristics and those which have semiconducting or insulating characteristics. In any real intermetallic compound there is a superposition of the different types of interatomic bonding and the solids generally have appreciable semiconducting character if the dominant bond force is ionic or covalent.

In the case of semiconducting intermetallic compounds, those with strongly covalent bonds tend to conform closely in composition to the simple proportions given by the chemical formula. Compounds with an ionic component in the bonding tend to exist in the solid phase with various concentrations of vacant lattice sites, interstitials or place exchange. These have a profound effect upon the electrical properties of the solid. The equilibrium concentrations of these defects have been discussed for a few representative compounds. In spite of the many intermetallic compounds being prepared today only a few of them have detailed information on phase diagrams in the vicinity of the stoichiometric composition.

Finally, in intermetallic compound semiconductors, the concentration of electrons and holes is often a complicated function of the phase-equilibrium relationships and is highly sensitive to temperature. The means by which changes occur in the solid fortunately depend upon a diffusion process which, at ordinary low temperatures, is excessively slow. Crystals prepared at high temperatures, to a desired composition, can be quenched to low temperatures where their composition is for all practical purposes fixed.

In a few intermetallic compound semiconductors, principally those with highly covalent interatomic forces, the composition is, essentially, fixed at the stoichiometric composition.

### References and Notes

1. W. Hume-Rothery, *J. Inst. Metals* **35,** 309 (1926).
2. K. F. Hulme and J. B. Mullin, *Solid State Electronics* **5,** 211 (1962).
3. The Hall effect is the transverse voltage developed in a conductor carrying a current perpendicular to a magnetic field. Its sign is the sign of the current carrier and its magnitude depends upon the concentration of these electrons or holes.
4. R. F. Brebrick, *J. Phys. Chem. Solids* **18,** 116 (1961).
5. W. W. Scanlon, *Phys. Rev.* **126,** 509 (1962).

---

# Lethal Genes and Analysis of Differentiation

## In higher organisms lethal genes serve as tools for studies of cell differentiation and cell genetics.

Salome Gluecksohn-Waelsch

Among the many problems of genetics untouched by recent spectacular advances in molecular genetics is that of lethal genes. The reasons for this lie primarily in the fact that lethal-gene problems touch upon various areas of genetics all of which are concerned with gene effects on levels more or less removed from that of primary gene action. Among these areas are population genetics, radiation genetics, and developmental and physiological genetics.

The analysis of gene action at the molecular level stops necessarily at a point where the interaction of genes, of gene products, of cells, and of tissues begins—in short, at the phenotype level. It is, on the other hand, precisely at this level that problems of cell, tissue, and organ differentiation make their appearance, and that those phenomena occur which serve to characterize a gene as a lethal. Even further removed from the molecular level of gene action are problems of lethal genes in populations, and of their origin, whether spontaneous or induced—for example, by radiation.

Because of the great significance of lethal genes in populations, because of their importance in studies of radiation genetics, and because of their role in the analysis of development and differentiation of higher organisms, it appears worth while to attempt at this time a re-evaluation of this problem and to relate it to new concepts of genetics.

In this attempt emphasis will be put on the physiological genetics of lethal genes. The significance of lethal genes in populations has been the subject of numerous discussions (*1*); an extensive literature deals with studies of radiation-induced lethals (*2*). These topics are not taken up here. Problems considered in this article include the mode of action of lethal genes, the properties that distinguish them from other mutant genes, the physiology of the effects of lethal genes, and their utilization in analyzing cell, tissue, and organ differentiation in higher organisms.

---

The author is professor of genetics at the Albert Einstein College of Medicine, New York, N.Y. This article is dedicated to Professor L. C. Dunn in friendship and admiration.