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SEMICONDUCTOR ALLOYS

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Since a good deal of experimental and theoretical effort is now being devoted to the study of semiconductor alloys, it seems appropriate to review the present status of the subject. The bulletin begins with a brief discussion of the atomic structure of disordered alloys. The nature of one-electron energy levels in alloys is then treated in some detail, and this is followed by a discussion of the lattice vibrational spectrum of alloys. In the remaining sections, representative experimental data on various optical, electrical, thermal, and magnetic properties of semiconductor alloys are interpreted in terms of existing theories.

Perhaps the most significant work that has been done in recent years in this field is the concerted study of the germanium-silicon alloy system. This work has done much to elucidate the electronic structure, the optical behavior, and the electronic properties of alloys in general. There is considerable need for similar work on other alloy systems. The theory of disordered alloys is still in a rudimentary state, though it has already proved useful in interpreting actual experimental data. It seems clear that much additional theoretical work on alloys will be required before most of the experimental information can be fully exploited.

Introduction

The object of this bulletin is to review some of the recent work on crystalline semiconductors whose atomic structure is characterized by a substantial degree of disorder. Such substances are properly called semiconductor alloys. To be specific, the term *alloy* will be restricted to disordered crystals of the solid substitutional solution type. The ordered phases of alloy systems will be regarded as compounds (ordered stoichiometric crystals). Interest will be centered on the effect of disorder on various physical properties, notably the electronic energy level scheme, the lattice vibrational spectrum, and miscellaneous electrical, magnetic, thermal, and optical characteristics.

During the past decade a great deal of effort has been devoted to the study of semiconducting materials[1]. Until relatively recently, most of this activity has been concerned with silicon and germanium[2,3,4]. Much of the current pioneering work is being done on semiconducting compounds[5,6,7]. An extensive search for new semiconducting materials, crystalline and non-crystalline as well, is now under way in many laboratories. The search is motivated in part by the need for substances having optimum properties for particular device applications, in part by the hope of discovering materials with unusual physical properties, and in part by scientific curiosity.

As an outgrowth of the current interest in new materials, a number of laboratories have initiated research programs on semiconducting alloy systems. While the objective of discovering substances with unique or desirable properties has not always been realized, these investigations have nevertheless provided a good deal of valuable information.

From a scientific standpoint, the most significant advance has been the work, both experimental and theoretical, on the germanium-silicon alloy system. Since the energy band structure of these alloys can be predicted tolerably well, it has proved possible to interpret, in satisfying detail, the observed variation with alloy composition of certain major electrical and optical properties.

In the present review, no attempt will be made to summarize the results of the numerous experimental investigations which have been carried out in recent years on diverse semiconducting alloy systems. However, adequate references will be given so that the interested reader may trace down the original papers. The authors have adopted the view that it is better to indicate the present status of the theory of semiconducting alloys, and to illustrate the theory by typical examples, than to summarize vast amounts of experimental data, most of which, unfortunately, lacks suitable theoretical interpretation.

It is the hope that the appearance of this review will not only call attention to interesting but perhaps little-known work, such as that published recently in the Russian literature (see Table I below), but will also stimulate further research activity on semiconducting alloy systems.

Atomic Structure[8]

There is a fundamental distinction between ordered and disordered crystals, just as there is a basic difference between crystalline and non-crystalline solids. In an ideal ordered crystal, the constituent atoms are arranged in space in the form of a regular array, with the proper type of atom occupying each lattice site. Such solids necessarily satisfy a stoichiometry requirement, and exhibit both long and short range order. Substitutional alloys (interstitial alloys will not be considered here) resemble ordered crystals in that the equilibrium positions of all the atomic nuclei form – very nearly – a regular lattice. In such alloys all the normal lattice sites are occupied, with the solute atoms replacing the solvent atoms at some of these sites. The disorder in alloys results from the essentially random arrangement of the solute atoms among the available lattice sites.

In crystalline substances, both ordered and disordered, there is long range order in the sense that the positions in space occupied by atoms form a lattice. Of course the identity of the atoms must be ignored when dealing with disordered crystals from this point of view. On the other hand, there is no such long range order in non-crystalline (amorphous) materials. In the thin amorphous films[9] obtained by evaporation, however, there is usually some degree of short range order present. [The

TABLE I

Mixed Crystals

Chemical Formula	Reference	Chemical Formula	Reference
$Mg_2Ge - Mg_2Sn$	a	$Tl_2Se - Sb_2Se_3$	g
$HgS - HgSe$, $HgSe - HgTe$	b	$As_2Se_3 - Sb_2Se_3$	h
$HgTe - HgS$		$Tl_2Se - [As{:}Sb]_2Se_3$	
$InAs - InSb$	c, d	$Ga_2Se_3 - ZnSe$	i
$InP - InAs$, $GaP - GaAs$	e	$Ga_2Te_3 - ZnTe$	
$InSb - GaSb$	d, f	$ZnS - ZnSe$	j
$InSb - AlSb$, $GaSb - AlSb$	f	$[Zn{:}Cd] - [S{:}Se]$	k
$GaAs - GaSb$, $GaAs - InAs$	d		

a. G. Busch and U. Winkler, *Helvetica Physica Acta* **26** 578-583 (1953).

b. E. I. Nikol'skaya and A. R. Regel', *Zhur. Tekhn. Fiziki* **25** 1347-1351, 1352-1356 (1955) [In Russian].

c. C. Shih and E. A. Perretti, *J. Amer. Chem. Soc.* **75** 608- (1953); *Trans. Amer. Soc. Metals* **46** 389-396 (1954); *Trans. Amer. Soc. Metals* Preprint **48** (45) (1955).

d. N. A. Goryunova and N. N. Fedorova, *Zhur. Tekhn. Fiziki* **25** 1339-1341 (1955) [In Russian].

e. O. G. Folberth, *Zeits. fur Naturforschung* **10a** 502-503 (1955).

f. W. Köster and B. Thoma, *Z. Metallkunde* **46** 293- (1955).

g. B. T. Kolomiets and N. A. Goryunova, *Zhur. Tekhn. Fiziki*, **25** 984-994 (1955) [In Russian].

h. N. A. Goryunova and B. T. Kolomiets, *Zhur. Tekhn. Fiziki*, **25** 2069-2078 (1955) [In Russian].

i. N. A. Goryunova, V. A. Kotovich, and V. A. Frank-Kamenetskii, *Doklady Akad. Nauk S.S.S.R.* **103** 659-662 (1955); N. A. Goryunova, V. S. Grigor'eva, B. M. Konavalenko, and S. M. Ryvkin, *Zhur. Tekhn. Fiziki* **25** 1675-1682 (1955) [In Russian].

j. see references 18, 19, and 20 of Section I.

k. H. W. Leverenz, E. J. Wood, R. E. Shrader, and S. Lasof, in G. R. Fonda, ed., PREPARATION AND CHARACTERISTICS OF LUMINESCENT MATERIALS, John Wiley and Sons, New York, 1948.

same statements hold for liquid[10] semiconductors.] In the case of amorphous germanium[11], each atom is found to have four nearest neighbors at 2.40 A and twelve next-nearest neighbors at 3.95 A, with an essentially random atomic distribution beyond second neighbors. These numerical values are virtually identical to those in single crystal germanium. [In contrast, each atom in liquid germanium[12] has eight nearest neighbors at 2.70 A, and there is a random arrangement beyond this distance.] The basic difference between disordered crystals and amorphous solids may be stated as follows: In the former, there is a correlation in the relative positions of different atoms – the identity of the atoms being ignored – for all orders of neighbors; in the latter, there is no correlation beyond a certain order of neighbor.

The distinction between disordered crystals and amorphous solids just stated has a number of important physical consequences. For example, the one-electron energy spectrum and the lattice vibrational spectrum of disordered crystals may be characterized by a Brillouin zone structure, though the reduced wave vector concept has a more restricted meaning than in ordered crystals. Since amorphous materials have no periodicity properties whatever, there is no associated reciprocal lattice, and hence a description of electronic and vibrational quantum states in terms of the zone schemes seems inappropriate. While some of the work to be discussed in subsequent sections has a bearing both on crystalline and non-crystalline materials, the major emphasis will be on the former.

For the purposes of classification, it is convenient to subdivide semiconductor alloys into the following categories:

(a) Lightly Doped Ordered Crystals

This class includes nearly perfect crystals having impurity concentrations so small that the individual impurity atoms can be treated independently. If the solute atoms (in substitutional alloys) have a different valency than the solvent atoms they replace, there will usually be localized donor or acceptor states associated with the solute atoms. On the other hand, if the solute and solvent atoms have the same valency, as in germanium-silicon alloys, localized electronic states having energy levels in the forbidden band are less likely to occur. Since the effect of the impurity atoms on the properties of the host crystal can be treated by perturbation methods, the theory of lightly doped ordered crystals has reached a high state of development. The same is true for the crystals in the next class.

(b) Slightly Disordered Crystals.

If the constitution of a crystal deviates from the ideal form due to the presence of vacancies and/or interstitials in limited numbers, rather than the presence of foreign atoms, the crystal belongs to this category. There will usually be localized donor or acceptor states associated with the vacant lattice sites or the interstitial host atoms. It is often possible to produce vacancy-interstitial pairs by irradiating[13] perfect crystals, or by synthesizing crystals under carefully controlled conditions[14].

(c) Heavily Doped Ordered Crystals

Included in this category are crystals having impurity concentrations so great that the various impurity atoms can no longer be dealt with separately. For convenience, this class of materials will be restricted to the case of solute atoms having a valency different from that of the solvent atoms they replace. The new feature which arises here is the merging of impurity levels into bands, or what amounts to the same thing, the interaction of neighboring impurity atoms. The theory of impurity bands is still in an early stage of development. This circumstance may be traced to the inherent mathematical difficulties, and also to the lack of clean-cut experimental results capable of guiding the theory.

(d) Mixed Crystals

This category differs from the previous one in two respects: First, it contemplates a wider composition range; secondly, the corresponding solute and solvent atoms here must have the same valency. In most cases this stipulation will be equivalent to the condition that the presence of the solute atoms does not lead to the creation of localized donor or acceptor states. Only if this latter condition is fulfilled can there be semiconducting alloys over a wide composition range. If the impurity concentration in case (c) is too great, the impurity bands may become so broad that there is no longer any forbidden band, and the crystal will behave more like a metal than a semiconductor. In the present case, (d), a similar valency does not insure a wide range of solubility; there are also factors such as ionic radius and electronegativity differences to consider. However, if a wide solubility range exists, it is likely that the system will be semiconducting over the whole of this range.

Perhaps the two simplest examples of mixed crystal systems are the binary systems *Ge-Si*[15] and *Se-Te*[16]. Stöhr and Klemm[15] showed that *Ge* and *Si* were miscible in all proportions, and noted that the lattice constant varied monotonically from that of silicon (5.430 A) to that of germanium (5.657 A). This curve is shown in Fig. 1, with some later data of Johnson and Christian[17] included. X-ray analysis[18] indicates that the *Ge* and *Si* atoms are arranged at random at the sites of a diamond-type lattice over the entire composition range. There is no X-ray evidence[18] for the presence of interstitial *Ge* or

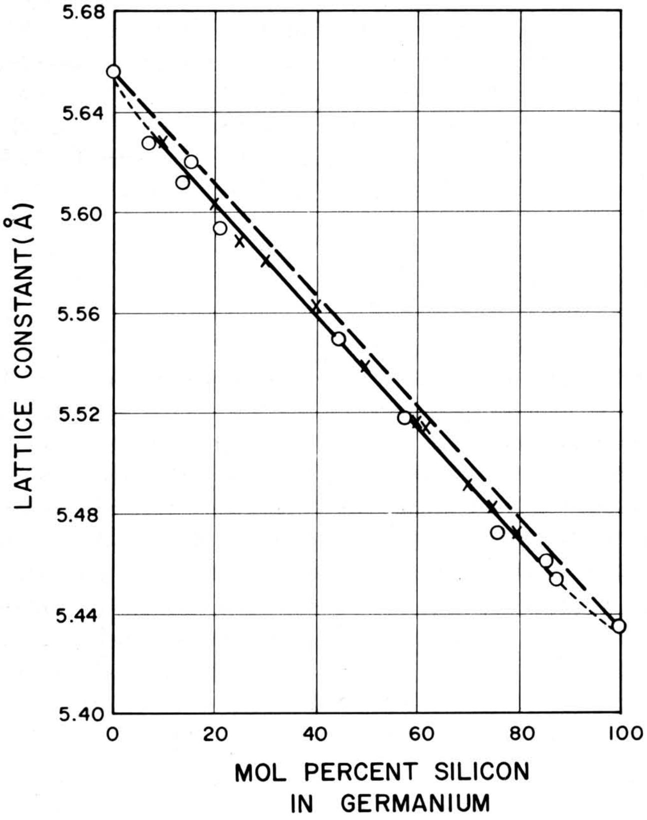

Fig. 1 – Variation of lattice constant of germanium-silicon alloys with mol percent silicon. x= Values given by Stöhr and Klemm (Ref. 15) corrected to the more modern values of lattice constant for pure germanium and silicon. o= Values of lattice constant measured and reported by Johnson and Christian (Ref. 17). [After Johnson and Christian]

Si atoms. Analogous studies of the Se-Te system have been carried out by Grison[16], who showed that Se and Te are mutually soluble in any concentration.

In a mixed crystal of the ternary type, such as ZnS-$ZnSe$[19,20,21] the Zn atoms form one sub-lattice, while the S and Se atoms are arranged at random on another sub-lattice. In a quaternary alloy such as ZnS-$CdSe$[19], the Zn and Cd atoms are randomly arranged on one sub-lattice, and the S and Se atoms are similarly dispersed on another. Listed in Table I are some mixed crystal systems involving three or more constituent atomic species which have been studied experimentally and which have come to our attention. No attempt has been made to compile a complete list of known mixed crystal systems; the contents of Table I should be regarded as representative, rather than exhaustive, especially in the case of the Russian work.

One of the most interesting features of mixed crystal systems is the relationship between crystal structure and composition. In the case of isomorphous components (substances having the same crystalline form and similar chemical formulae), the same crystal structure will usually persist at all concentrations. However, if one or more of the ingredients can crystallize in more than one crystal form – this situation is described by the term *polymorphism* – the structure of an intermediate alloy may depend upon the composition, as well as upon the method of preparation. For example, pure ZnS can exist in a number of distinct crystal forms[22] the cubic (sphalerite) and hexagonal (wurtzite) modifications being the most common. Asano[21] has shown that mixtures of ZnS and $ZnSe$ form cubic solid-solutions in any proportion as long as they are crystallized at 850 degrees C. The lattice constant varies linearly with composition (see Fig. 2). In contrast, for a crystallization temperature of 1100 degrees C, the predominant crystal structure tends to be hexagonal up to about 30 mol percent $ZnSe$; beyond this proportion the cubic form is the more common. Similar studies on other mixed crystal systems have been reported (see references to Table I).

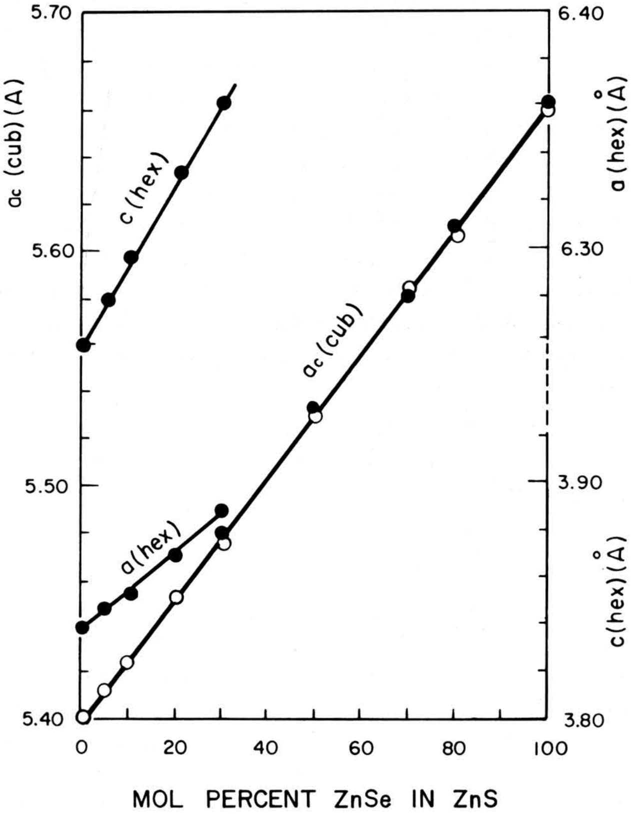

Fig. 2 – Variation of lattice constant of ZnS-$ZnSe$ mixed crystals with mol percent $ZnSe$. The open circles represent samples prepared at 850°C, while the heavy dots represent samples prepared at 1100°C. [After Asano, Ref. 21]

One-Electron Energy Levels

A number of attempts to calculate the electronic energy level distribution in disordered crystals have been made in recent years. A good deal of useful qualitative information has already been obtained by the examination of idealized one-dimensional alloys. Some inroads into the more difficult problem of a realistic three-dimensional alloy have been made with the aid of perturbation techniques. In the present section we will survey some of the recent theoretical work on alloys, emphasizing those conceptual aspects which are particularly pertinent to semiconducting alloys.

As is well known, the problem of determining the energy levels of electrons in a perfect crystal is greatly simplified by the translational symmetry of the crystal. In fact, it is possible to obtain an eigensolution valid for the entire crystal volume merely by solving the appropriate wave equation within a single unit cell. Since this simplification can no longer be made in the case of a disordered crystal, it is much more difficult to study a disordered crystal than an ordered one.

In a perfect crystal, the electronic energy levels fall naturally into well-defined bands. The transition from an allowed to a forbidden band of energies is abrupt. Within a given band, each quantum state is characterized by a reduced wave vector $\mathbf{k}$. This follows from the fact that $\mathbf{k}$ is a constant of the motion, or, as it is often expressed, $\mathbf{k}$ is a "good" quantum number. Much of the theoretical work to be described below has been concerned with determining the extent to which the concepts of allowed bands, forbidden bands, and quantum states characterized by $\mathbf{k}$ carry over to the case of disordered crystals.

James and Ginzbarg[23] and Landauer and Helland[24] approached the problem by constructing an idealized one-dimensional random alloy, and then determining the energy level distribution by numerical methods. It was found that the presence of disorder tends to smear out the transition regions between allowed and forbidden bands, so that the density of states decreases gradually, rather than abruptly, in the passage from allowed to forbidden bands. While these direct calculations provide a useful qualitative picture of the effect of disorder on the energy level distribution, they provide no general rules for the one-dimensional case, and, more seriously, they cannot be extended in an obvious manner to the practical case of three-dimensional alloys.

Various authors, including Saxon and Hutner[25], Luttinger[26], Kerner[27], Hart[28], and des Cloizeaux[29], have treated idealized one-dimensional alloys by analytical rather than numerical methods, in the hope of formulating general principles relating to the energy level distribution. Some progress has been made in the direction of answering such questions as the following: What is the probability that a given energy in a binary alloy AB is allowed (forbidden) if the corresponding energy in the pure constituents A and B is allowed (forbidden)?

While the above mentioned one-dimensional studies are instructive, they do not provide the type of quantitative information – such as the detailed form of the transition regions – that is essential to the analysis of three-dimensional alloys. In particular, there is reason to believe that the nature of the transition region depends upon the dimensionality of the crystal, so that the results for one-dimensional cases are not directly applicable to two- or three-dimensional cases. For information pertinent to three-dimensional problems, it is necessary to turn to the early work of Nordheim[30] and Muto[31], and to the more recent work of Parmenter[32-34], all of which are based on perturbation methods. Since some of this work employs Nordheim's virtual crystal model of an alloy, it is desirable to introduce the virtual crystal concept at this point.

Consider an aggregate of atoms arranged at random on the sites of some periodic lattice. The potential acting on an electron moving through the disordered alloy formed by the random configuration of atoms can be decomposed into a periodic part and a non-periodic part, as follows:

$$V_{alloy}(\mathbf{r}) = V_{periodic}(\mathbf{r}) + V_{non\text{-}periodic}(\mathbf{r}) .$$

The decomposition is carried out in such a manner that the periodic part is the average of the alloy potential over all possible random configurations of atoms in the alloy consistent with the given composition of the alloy. $V_{non\text{-}periodic}(\mathbf{r})$ is then the deviation of $V_{alloy}(\mathbf{r})$ from its average, $V_{periodic}(\mathbf{r})$. In a given alloy, the non-periodic part will have a form which depends upon the specific arrangement of the atoms, while in an ensemble of alloys of given composition the non-periodic part will have definite statistical attributes. The virtual crystal is defined by the periodic component, and the effect of disorder is represented by the non-periodic component.

Nordheim[30] used the virtual crystal concept in the course of a study of the residual resistance of alloys. He proceeded essentially by first order perturbation theory, regarding the virtual crystal potential $V_{periodic}(\mathbf{r})$ as the unperturbed potential, and the disorder potential $V_{non\text{-}periodic}(\mathbf{r})$ as the perturbing potential. Somewhat later, Muto[31] attempted to calculate the energy level distribution of an alloy on the basis of the virtual crystal viewpoint. Muto reasoned that the average over the Bloch functions of the virtual crystal is zero, so that there is no shift in the energy levels produced by disorder in the first order of perturbation theory. He suggested that a smearing of the band edges would take place in the second order of perturbation theory.

Subsequent work by Parmenter[32,34] extended the virtual crystal approach to the higher orders of conventional perturbation theory. Parmenter showed that the higher orders have only a minor effect on the energy level distribution near the middle of an unperturbed band. Near the top or bottom of an unperturbed band, however, the higher orders can have an important effect. In general, even orders of perturbation theory tend to raise or lower band edges according to whether the perturbing potential, $V_{non\text{-}periodic}(\mathbf{r})$, is predominantly repulsive or attractive, respectively. Odd orders of perturbation theory, other than first order, always tend to move the band edge out into the forbidden band, irrespective of the nature of the perturbing potential. The net effect is that band edges are smeared out into the forbidden bands. For three-dimensional alloys this smearing is always finite in extent so that the forbidden bands need not disappear altogether.

The contribution of second order perturbation theory to the smearing of a band edge can be seen from Fig. 3, taken from reference 32. In this figure ϵ is proportional to the energy and $d\eta/d\epsilon$ to the density of allowed states per unit energy. The parameter ϵ_o determines the shape of the energy tail extending into the forbidden band; e.g., $\epsilon_o = 0$ corresponds to a vanishing perturbation potential.

Under conditions that a perturbation approach is valid (see below), it is possible to label the quantum states in the disordered alloy by band indices and reduced wave vectors **k**. This follows from two considerations: (a) a conventional Brillouin zone scheme and conventional energy bands can be associated with the periodic virtual crystal potential; and (b) perturbation theory provides a bridge between the case of strict periodicity and the case of disorder in the limit of vanishingly small disorder. Although **k** is not really a good quantum number in a disordered alloy, however small the disorder, it can be used to label the quantum states in a restricted sense. To this extent, it can be employed[32] in connection with the determination of such quantities as the density of allowed states per unit energy, the expectation value of velocity of an electron, and the electron effective mass (the proportionality constant relating an externally applied force and the resultant acceleration of the electron).

In Fig. 4 are shown the $E(\mathbf{k})$ curves corresponding to some of the density-of-states curves of Fig. 3. An examination of the low-energy tail suggests that rather large velocities and rather small effective masses may result from the alloying in this energy region. While these effects tend to increase the electron mobility, they are probably offset by the incoherent scattering resulting from the disorder, so that the net effect would be a decrease in mobility with alloying, rather than an increase. A further effect which may be predicted theoretically[34]

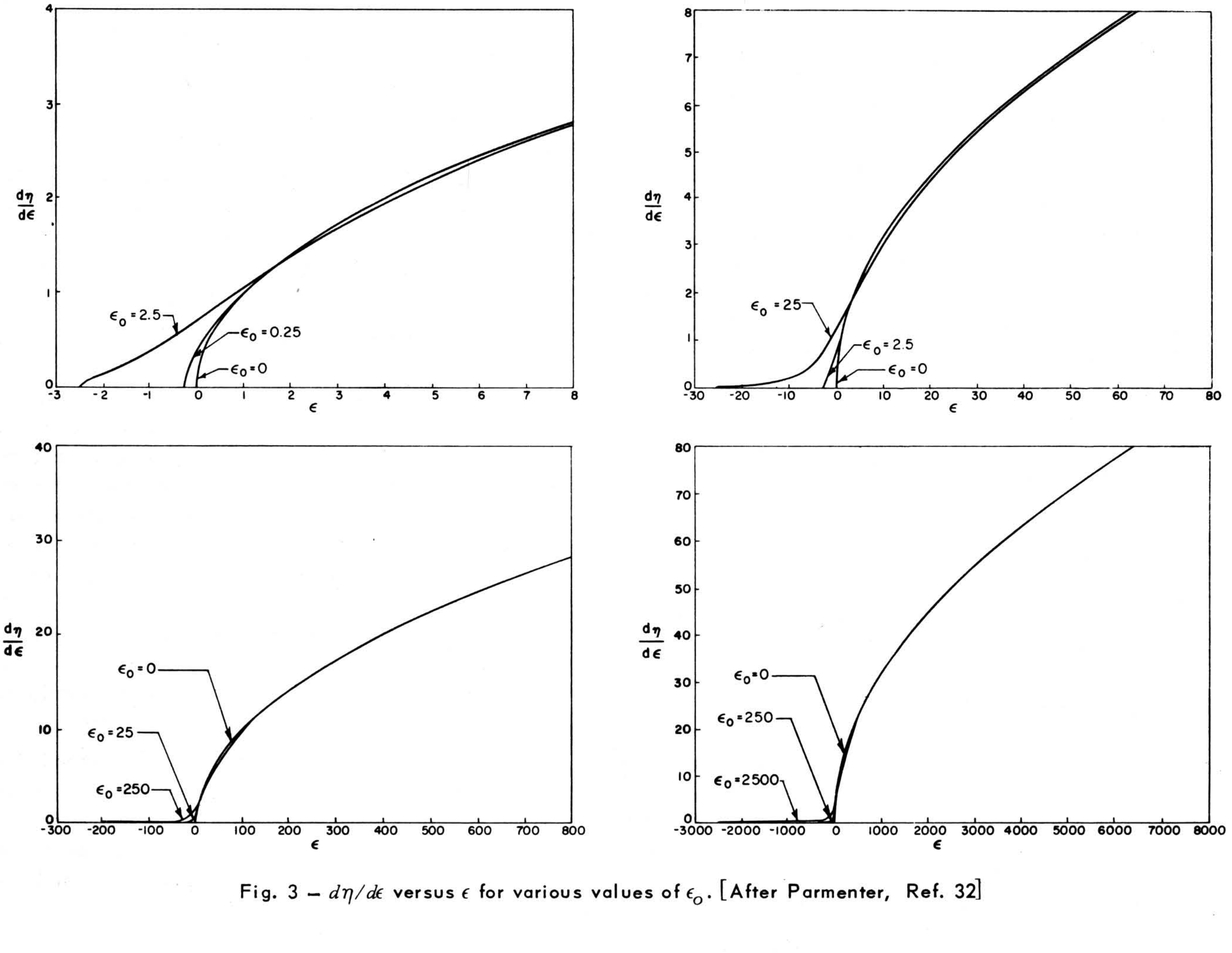

Fig. 3 – $d\eta/d\epsilon$ versus ϵ for various values of ϵ_o. [After Parmenter, Ref. 32]

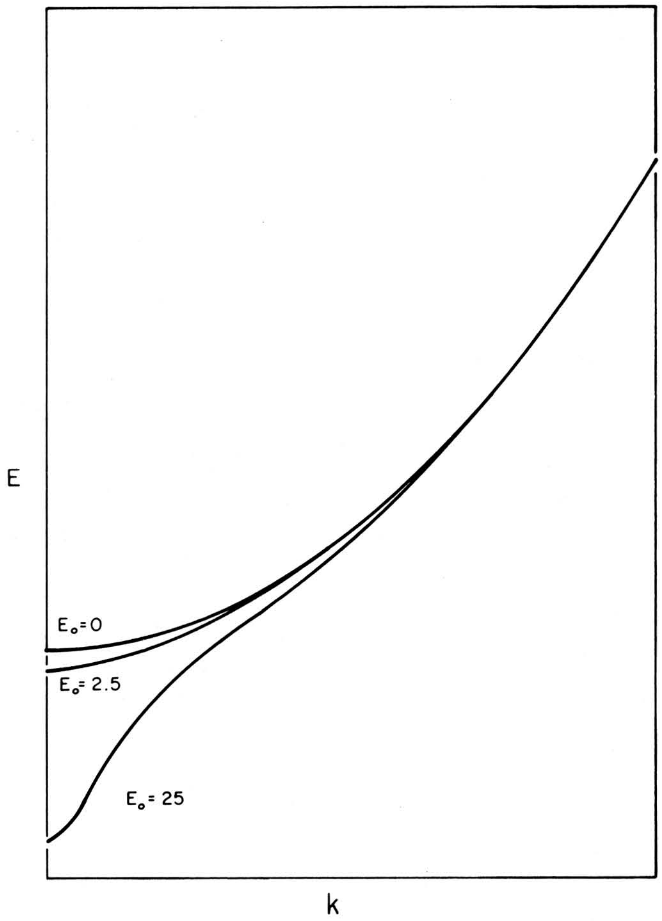

Fig. 4 – E versus k for various values of E_o.

is that, upon alloying, anisotropic effective masses at the bottom or the top of an energy band will become more nearly isotropic.

The virtual crystal approach leads to wave functions which can be misleading unless properly interpreted. In the case of a germanium-silicon alloy, for example, it is expected on physical grounds that a state near the bottom of the valence band have a wave function which resembles a germanium 4s atomic orbital in the neighborhood of germanium nuclei, just as this wave function should resemble a silicon 3s atomic orbital near the silicon nuclei. If the virtual crystal concept is misinterpreted, it might be thought that the nodal structure of wave functions is averaged in the same manner as the potentials, so that the state just considered would have a wave function with a nodal structure intermediate between germanium 4s and silicon 3s near all the crystal nuclei.

When properly interpreted, the virtual crystal approach requires that a given wave function have the appropriate nodal structure everywhere in space. A recent formulation by Parmenter[33], which, incidentally, is particularly suitable for actual numerical calculations, guarantees that the electronic wave functions behave properly in the vicinity of each crystal nucleus.

Muto's[31] utilization of non-degenerate perturbation theory, in conjunction with the virtual crystal model of a disordered alloy, has been criticized by James and Ginzbarg[23] on the ground that the perturbing potential mixes originally degenerate states together. While it is true that degenerate perturbation theory, rather than non-degenerate perturbation theory, must be employed when the calculation is restricted to a given order, Parmenter[32,33,34] has pointed out that the non-degenerate form is justified as long as one is prepared to carry the calculation to all orders of perturbation theory.

Under certain conditions, all of the states in the virtual crystal energy bands are modified only slightly by the presence of disorder. When this situation obtains, it is expected that all the states can be correctly represented by rapidly convergent perturbation-type expansions. If the presence of imperfections leads to a splitting-off of some states from the virtual crystal energy bands, the split-off states, and the remaining states as well, cannot be treated by perturbation methods, since the perturbation expansions diverge. When there is very substantial disorder present, the perturbing potential may be so large that a perturbation treatment fails. Such questions as these have received some attention[34], but deserve further study.

The electronic states which are split-off from the unperturbed energy bands by the presence of imperfections are of particular interest in semiconductors, since they form the donor and acceptor states. For sufficiently small impurity concentrations, the energy levels associated with these localized states will be sharp, and the associated density-of-states curve will be a delta function centered on the energy of these levels. As the impurity concentration increases, the impurity-level wave functions centered on neighboring impurity atoms will start to overlap, causing the originally sharp levels to spread into a narrow band of energies – the so-called impurity band.

A number of attempts have been made to study impurity bands theoretically, in particular, to determine the the density-of-states curve. The one-dimensional model of an impurity band studied by James and Ginzbarg[23] has already been mentioned. The main objection to this model is that it is one-dimensional, so that conclusions reached need not necessarily apply to three-dimensional problems. For example, there will always be at least one discrete state associated with an impurity atom in a one-dimensional problem, no matter how small the perturbing potential of the impurity is. On the other hand, small localized perturbing potentials do not necessarily give rise to discrete states in three dimensions.

A number of workers[35-38] have assumed that the impurity atoms form a super-lattice in the host crystal.

By this assumption, the problem is given spatial periodicity, so that a conventional energy-band solution may be obtained. Unfortunately, such an assumption removes one of the most important features of the problem – namely, the disorder. A three-dimensional model which attempts to take the disorder into account has been studied by Aigrain and Jancovici[39,40]. These authors obtained the expectation value of energy with respect to approximate, mutually orthogonal wave functions which were so constructed as to incorporate the disorder of the problem. It was possible to define a pseudo-quantum number $\mathbf{k}$, having the significance that the density-of-states curve could be obtained from the energy $E(\mathbf{k})$ in exactly the same manner as for an ordinary energy band.

The width in energy of a band formed by a superlattice of impurity atoms will vanish in an exponential fashion as f, the mol fraction of impurity atoms, goes to zero. This results from the nature of the overlap of the impurity-atom wave functions. On the other hand, the band width associated with a disordered set of impurity atoms will vanish much less rapidly with vanishing f. This difference in behavior results from the fact that the disorder admits of the possibility that two impurity atoms may be close together even when f is small.

In summarizing this section, it may be said that considerable progress has been made, particularly in recent years, in obtaining a conceptual understanding of the nature of electronic energy levels in disordered alloys. Despite this, much work remains to be done. For example, the present status of this work in no way compares with the advanced state of development of the theory of energy bands of a perfect crystal[41] – especially in regard to numerical calculations on specific systems. Concerning the even more difficult problem of energy levels in liquids[42,43] or amorphous solids[9], very little work has been done.

Lattice Vibrational Spectrum

The problem of determining the vibrational spectra of disordered crystals can be approached theoretically from several points of view. First, the disordered crystal can be replaced by the corresponding virtual crystal, and the spectrum of the latter can be calculated by standard methods. Next, an attempt can be made to obtain rigorous solutions for highly idealized models, and then infer from the results the nature of the solutions for more realistic cases. Finally, in the limit of extremely dilute alloys (very small amount of disorder), the problem can be treated in a variety of ways by perturbation methods. Some of the work which has already been done along these lines will be reviewed briefly below.

It should be noted at the outset that the problem of deducing the vibrational spectrum of an alloy is in many respects analogous to that of finding the spectrum of one-electron energy levels in an alloy. In each case there is an eigenvalue equation to be solved, and in each case the complicating factor is the presence of disorder. Information of a qualitative nature obtained by solving either problem is often directly applicable to the other. For example, just as certain interruptions in the crystal periodicity give rise to localized electronic states, so are particular structural imperfections expected to result in localized normal modes of vibration.

According to the virtual crystal approximation, an alloy is replaced by an equivalent perfect crystal in which each lattice site is occupied by the appropriate type of virtual atom. The force constants which enter into the dynamical theory must be taken as suitably averaged quantities. As an illustration of the method[44] consider a germanium-silicon alloy having the composition Ge_fSi_{1-f}. The virtual crystal is a diamond-type crystal, so that the results of Smith's work on diamond[45] can be employed. If attention is restricted to nearest-neighbor interactions, the dynamical matrices in Smith's theory can be expressed in terms of two force-constant to mass ratios, $(\alpha/M)_{alloy}$ and $(\beta/M)_{alloy}$. Each of these ratios depends, of course, on the composition (f) and has the same form; for example:

$$(\alpha/M)_{alloy} = f^2\,(\alpha_{GeGe}/M_{Ge}) + 2f(1-f)(\alpha_{GeSi})/(M_{Ge}M_{Si})^{1/2}$$
$$+\,(1-f)^2\,(\alpha_{SiSi}/M_{Si}),$$

where α_{ij} denotes the force constant between the nearest neighbors i and j; M_i is the mass of atom i; and f is the fraction of the lattice sites in the alloy occupied at random by germanium atoms. α_{GeGe} and α_{SiSi} can be determined from elastic data[46], and $\alpha_{GeSi} = \alpha_{SiGe}$ can be approximated by the arithmetic average of α_{GeGe} and α_{SiSi}. It is found[44] that the virtual crystal approximation predicts a substantially linear variation with composition of nearly all the normal modes of vibration, and hence of the lattice spectrum as a whole. There is as yet no experimental evidence with which this result may be compared.

A rigorous solution for the vibrational spectrum of a one-dimensional chain has been given by Dyson[47]. The chain is composed of point masses with nearest neighbors coupled by elastic springs obeying Hooke's law. Considering only longitudinal vibrations, and regarding the masses and strengths of the springs as random variables, Dyson derives in closed form an expression for the normal mode distribution. The result depends, of course, on the probability laws that are taken to represent the distributions of the masses and spring constants. Dyson's study of a special case suggests that as these distributions become wider and wider, the high frequency portion of the spectrum grows at the expense of the low frequency portion, and the upper extremity of the spectrum changes from a form having a sharp cutoff to one having a long tail.

Unfortunately, multi-dimensional problems do not appear amenable to treatment by the elegant formalism developed by Dyson for the one-dimensional case. About the best that can be done at present on the theoretical side is to consider multi-dimensional cases in the limit of vanishingly small disorder.

One of the first studies along these lines was that of Stripp and Kirkwood[48]. They investigated the vibrational spectrum and partition function of very dilute (three-dimensional) alloys by means of a powerful perturbation technique. A classical, close-packed, monatomic crystal served as the model, and the nearest-neighbor, harmonic approximation was employed in formulating the problem. The only defects considered were small numbers of vacant lattice sites. It was found that the influence of these vacancies on the thermodynamic properties increases in relative importance with the absolute temperature. Another interesting result was that a pair of vacancies will attract each other with an average force whose potential diminishes asymptotically as $1/R^3$, where R is the distance of separation of the vacancies.

Montroll and Potts[49,50] have also examined theoretically the effect of localized defects on the vibrations of a crystal. Their approach is somewhat more general than that of Stripp and Kirkwood, in that the localized defects can be impurity atoms and interstitial atoms as well as vacancies. Montroll and Potts[49] find (a) that the vast majority of the normal modes are perturbed only slightly by the presence of defects, and (b) that various types of defects can cause localized normal modes whose effect dies out rapidly with distance from the defect. These localized modes have vibrational frequencies which are displaced out of the frequency bands of the perfect crystal. In this respect they resemble localized electronic impurity states in semiconductors.

Montroll and Potts[49] also develop a theory of the interaction of two defects as a function of their distance of separation. The change in the zero-point energy of the crystal produced by the introduction of a defect pair was determined in the range of very low temperatures. The calculations show that like defects attract each other in a monatomic lattice. In their most recent paper[50], they also consider the interaction between localized defects and the boundaries of the crystal. They find that the defects will be attracted or repelled by the boundaries, depending upon the nature of the defects.

The lattice spectrum of a non-dilute alloy can be determined by experimental methods as well as by theoretical ones. In fact, certain experimental techniques seem ideally suited to the problem. The methods of temperature-diffuse X-ray scattering[51] and cold neutron scattering[52] have already proved their value in studies of metals and metallic alloys; if applied to semiconductor alloys they might yield valuable information. Investigations of the infrared lattice absorption and of the Raman effect are also likely to provide important information bearing on the lattice spectrum.

Optical Properties

In general, the intrinsic and extrinsic optical properties of a semiconducting alloy will depend upon (a) the nature of the electronic quantum states; (b) the nature of the lattice vibrational spectrum; and (c) the coupling between the electrons and the lattice vibrations. As long as ordering effects do not occur, these three factors may be expected to vary in a continuous manner with composition in a given alloy system. Therefore, a continuous variation of the optical properties with composition is anticipated.

This expectation is generally borne out by the experimental results (see references in Table I). For example, the threshold for fundamental absorption (due to electronic transitions across the forbidden band) is found to shift gradually with composition in a number of alloy systems, including the following: *Ge-Si*[17,53,54]; *Se-Te*[55]; *InP-InAs*[56]; and *GaP-GaAs*[56]. For the *Ge-Si* system, data are available over the entire composition range, while in the other three cases some ranges have not yet been examined. In some systems, notably *Ge-Si* and *GaP-GaAs*, the rate of change of the absorption edge with composition has markedly different values at different compositions. While a gradual variation in the rate of change does not call for any detailed explanation, a "discontinuity" of the type observed in the *Ge-Si* system (see below) needs an interpretation.

Because of this unusual behavior, it is instructive to consider the *Ge-Si* alloys in some detail. In Fig. 5 is shown the experimental data for the variation of the optical gap with composition, as reported by Johnson and Christian[17]. Note that the curve exhibits a marked change in slope in the neighborhood of 15 atomic percent silicon. In order to explain this unexpected behavior, it is necessary to consider the energy band structure of the separate components, and of the intermediate alloys (see Fig. 6).

For both germanium and silicon, the valence band edge (i.e., absolute maximum) occurs at the central point of the reduced zone. The conduction band edge lies along the [111] and the [100] axes of the reduced zone in germanium and silicon, respectively. Since a good deal about the band structure of the two extremes is known[2,3,4], including the gross topology of the lowest conduction bands and the highest valence bands, it is a relatively simple

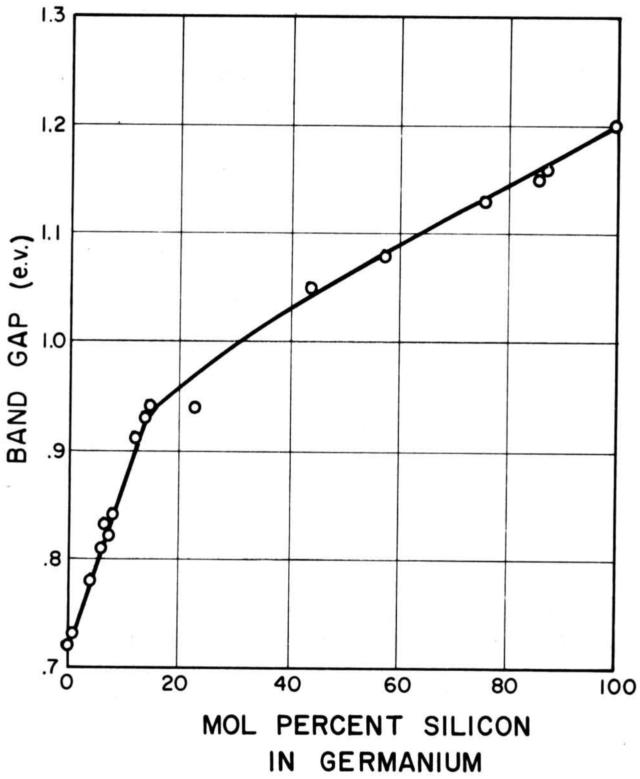

Fig. 5 – Variation of the energy gap in germanium-silicon alloys with mol percent silicon, as determined by optical absorption measurements. [After Johnson and Christian, Ref. 17]

matter[57] to predict what sort of change in the band structure with alloying would lead to the experimental results shown in Fig. 5. For example, it may be inferred from the results of some theoretical work[58] that the valence band edge remains at the central zone point over the entire composition range, and, further, that the major changes occur in the conduction band structure. Of course the spin-orbit splitting between certain pairs of bands will vary with composition, but this feature is of no real importance for the problem at hand.

As silicon atoms are substituted for germanium atoms, the three types of minima in the lowest conduction band of germanium (see Fig. 6c) move away from the highest valence band state, but at different rates. The [000] minimum rises most rapidly, and the [100] minima least rapidly, the motion of the [111] minima being intermediate. For the moment, the role that phonons play in assisting the optical absorption will be ignored, and the intermediate alloys will be treated in terms of their virtual crystals. The threshold for absorption is then determined by the energy separation between the top of the valence band and the bottom of the conduction band, irrespective of the location of the latter in the reduced zone.

On the basis of these remarks, it is clear that the rapid change of the optical gap in the range 0 to 15 atomic percent silicon can be attributed to the rapid motion of the [111] minima relative to the valence band edge. At about 15 percent, the [111] minima rise above the [100] minima, and the relatively slow change in the remaining composition range is due to the slower motion of the [100] minima. In going from pure germanium to pure silicon, the conduction band electrons first occupy states only near the [111] minima, then near both the [111] and the [100] minima, and finally only near the [100] minima. The conduction band edge switches its location in the reduced zone at some critical composition, which, according to the experimental evidence[17], is approximately 15 atomic percent silicon. While the [111] and the [100] minima are within a few kT of each other on an energy scale, states near both types of minima will be occupied.

As has already been mentioned, the valence and

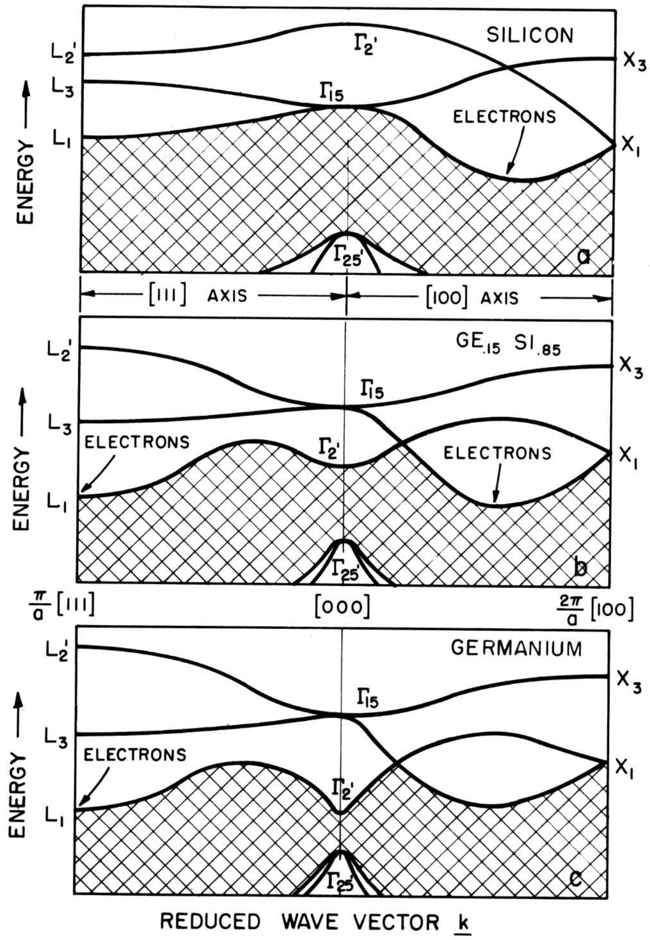

Fig. 6 – Schematic diagrams of electronic energy bands of (a) pure silicon, (b) germanium-silicon alloy, composition $Ge_{.85}Si_{.15}$, and (c) pure germanium. For reasons of simplicity, the spin-orbit splitting is not shown. In all three cases, the top of the valence band is at the central zone point. In (a) and (c), the bottom of the conduction band lies along the [100], and the [111] axes, respectively. In (c), the [000] minimum and the [100] minima lie *0.10* and *0.18 ev* above the [111] minima, respectively. In (b), the bottom of the conduction band occurs along both the [100] and the [111] axes. Symbols such as X_1 denote the symmetry classification of the electronic states, in the conventional group theoretical notation. [After Herman, Refs. 4, 57, and 58]

conduction band edges in *Ge-Si* alloys occur at different positions in the reduced zone over the entire composition range. Since optically induced electronic transitions involving a change in **k** require the assistance of phonons, a detailed study of the optical absorption as a function of composition must take into account not only the change in band structure with alloying, but also the corresponding changes in the lattice spectrum and in the electron-phonon coupling.

Detailed measurements of the fundamental optical absorption in *Ge-Si* alloys have been carried out by Braunstein[53] and by Moore[54]. Using the phenomenological theory of MacFarlane and Roberts[59] as a guide, Braunstein and Moore are able to determine the composition dependence of the forbidden band width to a high degree of precision. Their results agree qualitatively with those reported previously by Johnson and Christian[17]. In addition, Braunstein and Moore are able to deduce the frequencies of the phonons which assist the non-vertical electronic transitions. The variation of these phonon frequencies with composition lends further credence to the theoretical interpretation[57] of the optical behavior. Finally, Moore[54] has examined the effect of alloying upon the absorption due to vertical (**k**-conserving) electronic transitions, at the germanium-rich end of the range. He found that the motion of the [000] minimum is roughly twice as rapid as that of the [111] minima, a result which is consistent with the theory[57].

In summary, it might be observed that a study of the intrinsic optical properties can shed considerable light on the energy band structure of an alloy system. The more that is known in advance about the band structure, the more can be deduced from a careful examination of the optical properties. If the band structures of the two extreme cases are known in sufficient detail, it will usually be possible to predict the intermediate behavior with the aid of symmetry arguments and topological considerations.

Let us now turn to some of the extrinsic optical properties, particularly the absorption and emission associated with electronic transitions to or from localized states due to the presence of impurity atoms.

Consider first an impurity atom having a ground state energy level which lies close (within a few hundredths of an *ev*) to the valence or conduction band edge. Since the associated electronic orbit will extend over many hundreds or thousands of atomic cells, this impurity state will not be greatly influenced by the particular host atoms which happen to be its immediate neighbors. In such cases, there will be only one donor or acceptor ground state over the entire composition range, and the energy level of this state will vary essentially continuously with composition. Interesting effects may take place if there is a switchover in the band structure bordering the impurity levels. For example, in the case of column V donors in the *Ge-Si* alloy system, there should be a change in the multiplet structure[60] and in the order of certain excited states as the critical composition (15 atomic percent silicon) is traversed.

For purposes of comparison, consider next an impurity atom having a ground state energy level which lies deep within the forbidden band, say at least a few tenths of an *ev* away from the nearest band edge. The electronic orbit will now be confined to relatively few atomic cells, so that the nature of the state will be strongly influenced by the particular host atoms which occupy positions adjacent to the impurity atom in question. Under such conditions, a multiplication in the number of ground states will occur as a sweep across the composition range is made.

This actually occurs in the emission spectrum of silver-activated zinc sulpho-selenides[20]. As *Se* is substituted for *S*, the original emission bands shift to longer wavelengths, and at the same time new emission bands appear which are also shifted to longer wavelengths with increasing *Se* content. The original emission bands are undoubtedly associated with a silver atom substituting for a zinc atom and having four sulphur atoms as nearest neighbors. On this interpretation, the new bands would arise from silver atoms having one or more selenium atoms as nearest neighbors. While the overall behavior is "continuous" in the sense that emission bands grow or decay very gradually with composition, it is certainly more complicated than the behavior in the previous example, where instead of a multiplicity of ground state impurity levels, there is only one.

The present state of our knowledge of the extrinsic optical properties of mixed crystals may be summarized as follows: In the case of crystalline phosphor materials, there is a large amount of experimental data available[19]. Most of these data were accumulated in the course of investigations where practical objectives were paramount. As a result of this situation, there exists a vast body of information which is extremely difficult to interpret theoretically, partly for lack of suitable theories, and partly for lack of precise information concerning the composition and structure of the materials in question. If progress in scientific directions is to be made, it seems essential that careful measurements be carried out on highly purified single crystals. This approach is bearing fruit in the case of the *Ge-Si* alloys[61], and should prove equally valuable for more complicated situations.

Transport Properties

The phenomenological treatment of the transport of charge and heat in semiconducting alloys is formally identical to the approach in pure crystals. A relaxation time representing the scattering of the appropriate carriers is assumed, and the electric or heat current obtained from the solution of the Boltzmann transport equation. The disordered alloy character introduces effects which must be included in the Boltzmann equation. Perhaps the most important of these is the modification in the relaxation time brought about by disorder. In those alloy systems which have been studied in detail, the experiments indicate a variation of the carrier relaxation time with the degree of alloying. Under certain conditions, the disorder scattering can become the dominant scattering mechanism.

The transport properties will also be affected by changes in the electronic and vibrational quantum states, whether they are due to a variation of the virtual crystal with composition in a given alloy system, or to the presence of disorder. Unfortunately, it is difficult to separate these two classes of quantum state changes by conventional experiments. The experimental data on the germanium-silicon alloy system can be successfully interpreted in terms of virtual crystal changes alone.

Virtual Crystal Effects

As has been noted, an alloy can be represented by a virtual crystal, which by definition is strictly periodic. It follows from the definition, that an energy band structure can be associated with the virtual crystal, and hence with the alloy itself. It must be borne in mind, however, that the presence of disorder tends to blur the form of the band structure. In spite of this blurring, the virtual crystal band structure remains a good first approximation to the electronic energy level distribution. The object of this section is to present experimental evidence, gathered from diverse studies of transport phenomena, supporting this statement.

Cyclotron resonance absorption measurements[62] have provided detailed information about the band structure of germanium and silicon, particularly the shape of the energy surfaces near the bottom of the conduction band and the top of the valence band. These experiments were carried out at microwave frequencies (in the range 1 to 5×10^{10} cycles per second) and required samples with long scattering relaxation times τ ($\omega\tau \geq 1$) to show appreciable absorption at the resonant magnetic field value. Some crystals from the germanium-silicon alloy system have also been studied[63] by this technique. Surprisingly enough, resonance was observed with as much as 5 percent silicon in germanium, whereas 10^{-5} percent of column III or column V impurities usually results in too small a value of τ for resonance to be resolved. The relaxation times in the alloys were in the range 1 to 4×10^{-11} second. Studies at 4.8×10^{10} cycles per second were limited to alloys of less than 5 percent composition because of the decreasing relaxation time with increasing alloying.

Alloys of 0.9 and 5.4 percent silicon in germanium exhibited the band structure of germanium. At the other end of the system, at least 1 percent germanium in silicon does not change the band structure from that of pure silicon. The effective masses in the alloys were within experimental error of the values found for the pure crystals. The theoretically predicted changes[34] in the effective masses in germanium lie within the experimental errors of both the germanium and the alloy measurements. Thus, the measurements do not disagree with the predictions of the theory.

It may be concluded from the cyclotron resonance observations that alloys of silicon with small amounts of germanium have a virtual crystal like the pure silicon crystal; similarly, alloys of germanium with small amounts of silicon have a virtual crystal like the pure germanium crystal. Since these observations do not extend beyond 5 percent alloy composition, they do not provide information about the behavior at intermediate compositions, in particular, at 15 percent silicon in germanium, where the the most interesting effects should occur.

D-C measurements may also give details of the band structure. Observations of the galvanomagnetic effects in germanium[64] and silicon[65] have been interpreted[65,66,67] to yield information on the electronic band structure. The magnetoresistance observed has a symmetry (with respect to the crystalline axes) which depends on the symmetry of the energy-momentum relations obeyed by the electrons. Fortunately, the electrons in germanium (with [111]-symmetry energy surfaces) have a magneto-

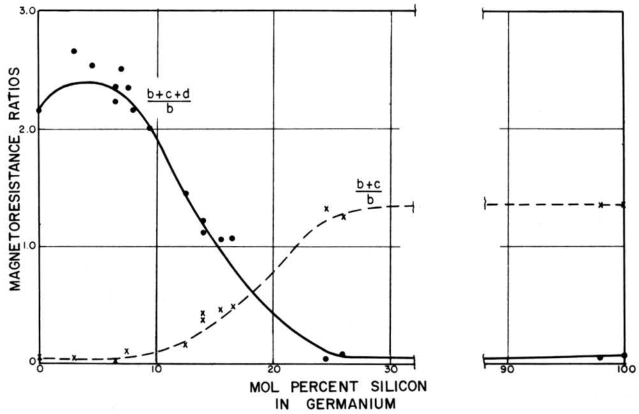

Fig. 7 — Magnetoresistance of germanium-silicon alloys as a function of silicon content. For energy surfaces with [111] symmetry, the function $b+c$ should be zero, while d depends directly on the deviation from spherical symmetry. Thus $b+c \ll b+c+d$ for [111] surfaces, as is the case for germanium. For energy surfaces with [100] symmetry, the function $b+c+d$ should be zero, with d again depending directly on the deviation from spherical symmetry. Thus $b+c+d \ll b+c$ for [100] surfaces, as is the case for silicon. [After Glicksman, Ref. 68]

resistance effect considerably different from that of the electrons in silicon (with [100]-symmetry energy surfaces). The combinations of observed magnetoresistance data[68] which bring out the differences in symmetry are plotted in Fig. 7. There is an obvious change in this symmetry in the region 10 to 20 percent silicon in germanium from the [111]-symmetry for the alloys of less than 10 percent silicon to the [100]-symmetry for alloys of greater than 20 percent silicon in germanium. In the 10 to 20 percent silicon in germanium. In the 10 to 20 percent silicon range, the data have been interpreted[69] as due to a sum of contributions from electrons in [111]-oriented energy minima and from electrons in [100]-oriented energy minima. These results substantiate the band structure suggested by Herman[57] for the alloys to explain the optical absorption experiments[17].

A combination of Hall and magnetoresistance measurements can be used to calculate the asymmetry of the energy surfaces[65,66,67], provided the relaxation time inintroduces no additional asymmetry. If this latter assumption is correct, the asymmetry in the effective mass of the alloys' [111] surfaces does not vary outside experimental error for alloys of composition from pure germanium to about 16 percent silicon in germanium[69]. The observations on alloys of 25 percent silicon in germanium give an asymmetry[68] in the [100] surfaces which is the same as that found in silicon, within experimental error. The galvanomagnetic observations on the germanium-silicon alloy system show that the lowest conduction band changes from that found in germanium to that found in silicon, at an alloy composition of about 15 percent. The character of the bands in the alloys seems quite similar to that found in the pure material.

The information available on other systems is not as extensive as that for the germanium-silicon system. Hall, Hedden, and Turner[70] have made use of their measurements of the variation of the conductivity of selenium-tellurium alloys with temperature to calculate the energy gap as a function of composition. Their first observations yielded an energy gap versus composition curve containing both a maximum and a minimum, this result has yet to be verified. Nussbaum[71] has measured the Hall mobility of alloys of up to 13 percent selenium in tellurium. There is no consistent variation of the data with alloy composition in that range. However, it was found that the Hall mobilities of holes in the alloys varied as $T^{-3/2}$. The complexity and corresponding lack of complete knowledge of the band structures of selenium and tellurium make the data difficult to interpret in terms of a consistent set of virtual crystals for the alloys.

The system *HgSe – HgTe* has been studied by Nikol'skaya and Regel'[72]. Their measurements of the Hall mobility of electrons in polycrystalline samples of the alloys could be fitted by a smooth curve, with an indication of a maximum toward the middle of the alloy range. Again lack of a frame of reference hampers an interpretation; knowing little about the band structure of the pure components, one can say nothing with confidence about the alloy behavior.

The Relaxation Time

In alloy systems, the relaxation time differs from that for a pure crystal because of the scattering of the carriers by the disorder present. This problem was considered by Nordheim[30], who calculated the scattering relaxation time τ for such random scattering in a metal alloy. It is instructive to compare this scattering with that caused by the thermal vibrations of the atoms in the lattice. In the alloy disorder case, Nordheim found that:

$$1/\tau = C_1 f(1-f) E^{1/2}$$

where E represents the energy, and where C_1 is a temperature-independent factor which includes the strength of the scattering and the effective masses of the electrons.

For thermal vibrations, the relaxation time is given by the following expression:

$$1/\tau = C_2 E^{1/2}$$

where C_2 includes the strength of the scattering and is proportional to the temperature. Since the two relaxation times have the same energy dependence, the mobility, Hall effect, and magnetoresistance can be easily calculated when both must be included. The reciprocal of the carrier mobility in a semiconductor alloy will then be the sum of two terms, one representing the disorder scattering, and the other the thermal lattice scattering. The former will vary with the concentration as $f(1-f)$, and with the temperature as $T^{1/2}$, whereas the latter will be proportional to $T^{3/2}$.

A somewhat different approach has been followed by Brooks[73] in considering the disorder scattering, with application to the germanium-silicon system. The potential function of the alloy is represented in terms of the band energies of the pure elements arranged at random. The scattering relaxation time has a form similar to the one quoted above, and the mobility has the same $T^{1/2}$ temperature dependence as noted above. Brooks estimated the parameters in his expressions from measured data on germanium and silicon. He predicted that the disorder mobility would equal the thermal mobility at room temperature for an alloy of 8 percent silicon in germanium.

Levitas[74] has measured the conductivity and Hall effect in the range 100 – 300 degrees K for p-type germanium-silicon alloys. Unfortunately, most of the samples were polycrystalline, with varying impurity concentrations, but the main features observed are significant. Levitas noted that the mobility decreased with alloying, and varied less strongly with temperature in the alloys (of less than 60 percent silicon) than in pure germanium or pure silicon. This is the behavior expected if the disorder scattering contributes to reducing the mobility, because the disorder mobility varies less strongly with the temperature than does the thermal scattering.

Some measurements by Glicksman[68] of the room temperature Hall mobility of electrons in germanium-silicon alloys are plotted as a function of alloy composition in Fig. 8. The alloy samples studied were n-type single crystals. Observations of the mobility between 80 and 300 degrees K for some of the samples (5 to 7 percent silicon) could be interpreted as a sum of contributions from thermal scattering and disorder scattering. At room temperature the disorder contribution was about equal to the thermal vibration contribution for an alloy of 9 percent silicon in germanium. This result is in good agreement with the values calculated by Brooks[73].

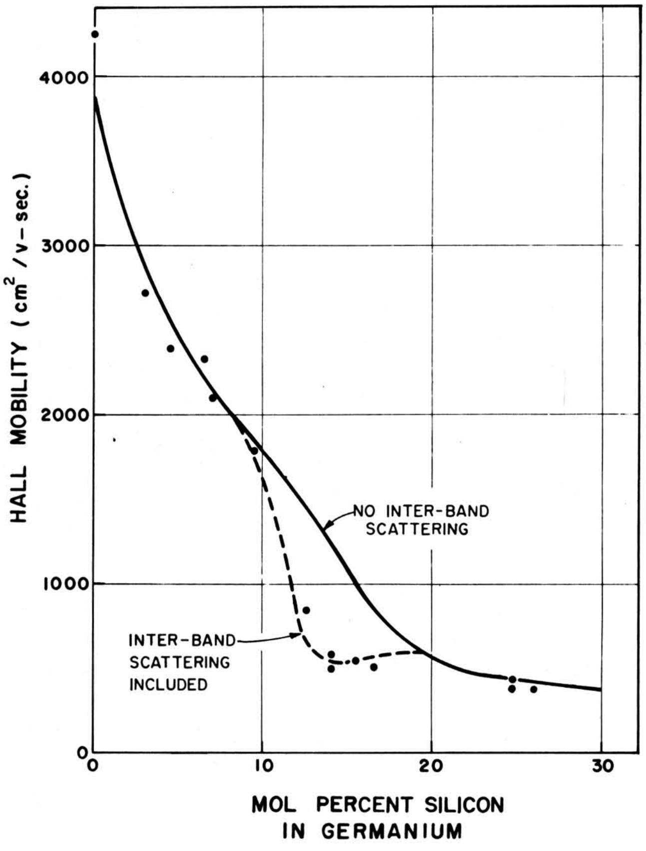

Fig. 8 – Hall mobility of electrons in germanium-silicon alloys as a function of silicon content. The curves are calculated for the two cases labelled; the circles are the experimental points. [After Glicksman, Ref. 69]

The solid curve in Fig. 8 is calculated using the above information to determine the strength of the disordering scattering. The change from the high mobility [111] minima to the lower mobility [100] minima causes the calculated decrease in the 10 to 20 percent region. However, the observed mobility in this two-band region is considerably lower than that represented by the solid curve. In order to fit the data, an additional scattering mechanism must be included which lowers the mobility when the two bands are close together. Inter-band scattering between the [100] family of spheroids and the [111] group may be the mechanism. This was suggested by Brooks and Paul[75] to explain the great decrease in mobility they observed in measurements of germanium and of germanium-silicon alloys under pressure. The application of pressure is believed to cause the [111] and the [100] minima to approach each other. The results of the calculations including inter-band scattering are shown in Fig. 8 as a dashed curve, which is a good fit to the data. The mobility in the alloys falls off with alloy composition just as is to be expected if due to disorder scattering, at least for the alloys where the conduction is almost entirely in one band.

Mobility measurements by Nussbaum[71] in the selenium-tellurium system showed no consistent variation with alloy composition; in particular, there was no strong decrease evident. It is possible that the failure to see disorder scattering is due to a thermal vibration scattering so large that it entirely masks the disorder scattering.

Folberth[56] has reported values of the Hall mobility in polycrystalline samples of *InAs-InP* alloys. The mobility drops rapidly from the *InAs* value of 20,000 cm^2/volt-sec to about 8000 cm^2/volt-sec for 20 percent *InP*, the latter value being about twice that observed in pure *InP*. Since the band structures of the individual components are as yet undetermined, the virtual crystal properties are unknown, and definite conclusions cannot be drawn from these data with regard to disorder scattering effects. Measurements on single crystals of higher purity in these systems should prove as enlightening as those made in the simpler alloy system of silicon and germanium.

Very little attention has been directed to the thermal properties of semiconductor alloys. One of the few papers which treats this subject is that by Joffe and Joffe[76], which reports results obtained for *Ge-Si* alloys, *Si-Sn* alloys, and *PbTe-PbSe* alloys. In all these cases it is found that alloying reduces the thermal conductivity considerably. For example, in the *Ge-Si* system the thermal conductivity is reduced from 0.145 cal/cm-sec-degrees K for pure germanium at room temperature to 0.008 cal/cm-sec-degrees K for an alloy with 50 to 60 percent silicon content. In the case of the *PbTe-PbSe* alloys, the thermal conductivity is independent of temperature over a considerable range below and above room temperature.

In order to explain these results, Joffe and Joffe assume that the transport of heat energy by the diffusion of phonons is the dominant mechanism governing the thermal conductivity. They then consider the factors determining the mean free paths of the phonons. Because phonons have rather short wavelengths, at least compared with the electrons or holes responsible for electrical conduction, their mean free path is much more sensitive to local deviations from the regular periodicity of the perfect crystal than is the mean free path of electrons of or holes. In an alloy, the disorder provides for abundant phonon scattering; the phonon mean free path in a 50 percent silicon-germanium alloy is of the same order as the atomic spacing. These considerations explain why the thermal conductivity is much more sensitive to alloying than is the electrical conductivity.

Concluding Remarks

Present efforts to interpret the properties of semiconducting alloys lean heavily on the results of the earlier investigations[8,77] of metallic alloys, especially in the crystallographic domain. From a structural standpoint, semiconducting and metallic alloys have much in common, and the similarities have been used to advantage in recent semiconductor work. For example, it has been presumed that the crystal structure of an intermediate (semiconducting) alloy would be isomorphous with those of the pure constiuents; and, further, that the lattice constant in an isomorphous series would vary uniformly with composition. While other possibilities are conceivable, the above conjectures have invariably been borne out by the experimental investigations.

The simplest approach to the theory of disordered crystals or alloys is the virtual crystal approximation, which, paradoxically, ignores the disorder altogether. According to this approximation, an alloy can be represented by a suitable virtual crystal whose form depends upon the alloy composition. The nature and distribution of the electronic and vibrational quantum states of a given alloy are determined in large measure by the constitution of its virtual crystal counterpart. The experimental evidence gathered to date suggests that the virtual crystal approximation is quite adequate for studying the composition dependence of the energy band structure of alloy systems. Refined theoretical treatments, which specifically take into account the effect of disorder, predict additional effects, such as the "tailing" of energy bands. Since these specific disorder effects have so far escaped experimental notice, they are apparently very small.

The germanium-silicon alloy system has been the main source of information concerning the variation of the energy band structure in alloys with composition. It has been possible to explore the band structure behavior as a function of composition in a rational manner, and to interpret the optical and galvanomagnetic data in considerable detail. The successful study of the germanium-silicon alloy system owes a great deal to the previous work on the pure constituents. It is probably a general rule that a detailed knowledge of the band structure of the separate components is a prerequisite to the successful exploration of the intermediate alloys.

The disorder in alloys has a number of important consequences, the most significant of these being the effect on the relaxation times of electrons, holes, and phonons. In general, the mean free paths of carriers will be reduced by the random deviations from strict periodicity. The reduction of the electrical and thermal conductivities with alloying has been observed in a number of alloy systems. In the case of the germanium-silicon alloys, the disorder contributes importantly to the scattering of electrons, reducing the electron mobility in the alloys to values well below those in the pure elements. A further reduction in the electron mobility takes place in the neighborhood of 15 percent silicon, where the conduction band is defined by two groups of energy minima, the [111] and the [100] groups. This further reduction can be explained in terms of inter-band scattering, a mechanism which has often been employed in the interpretation of the conductivity of transition metals and their alloys[77]. As already mentioned, the presence of disorder modifies the electronic energy level distribution, but this effect is small and the ultimate effect on the transport properties is probably smaller still.

There are numerous problems which cannot be solved for the case of concentrated alloys, but which can be readily solved in the limit of infinitely dilute alloys with the aid of standard perturbation methods. For example, in the theory of lattice vibrations, it can be shown that localized structural defects usually perturb most of the normal modes only slightly, and in addition, often give rise to localized normal modes near the defects. These latter are analogous to the bound impurity states of an electron in a semiconductor.

Relatively few semiconductor alloy systems have been studied so far, and the behavior of only one of these, the germanium-silicon system, can be explained in some detail. While many of the results obtained in these studies bear a close resemblance to the results for metallic alloy systems, some phenomena of common occurrence in metallic alloys have not yet been observed for semiconductor alloys. For example, order-disorder transitions have yet to be seen. The discovery of a semiconducting alloy exhibiting an order-disorder transition should prove very fruitful, because, for semiconductors, details of the energy band structure and carrier relaxation time are more directly available than for metals.

While much more information is required before every aspect of alloy systems is understood, the recent studies of semiconductor alloy systems have yielded a good deal of information. When these studies are fully interpreted, they should prove useful in furthering a general understanding of the solid state.

R. H. Parmenter

R. H. Parmenter

Maurice Glicksman

Maurice Glicksman

Frank Herman

Frank Herman

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