AFCRL-63-74

Final Report

INVESTIGATION OF SOLID STATE ELECTROLYTE

Prepared for:

AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS

CONTRACT NO. AF 19(604)-7231
PROJECT 5620
TASK 562001

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA   *SRI

407 809

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

February 4, 1963

AFCRL-63-74

Final Report

INVESTIGATION OF SOLID STATE ELECTROLYTE

Prepared for:

AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS

CONTRACT NO. AF 19(604)-7231
PROJECT 5620
TASK 562001

By: W. J. Fredricks   F. J. Keneshea   D. S. Bloom   A. B. Scott

SRI Project No. PAU-3225

Approved:

FELIX T. SMITH, DIRECTOR
DIVISION OF CHEMICAL PHYSICS

Copy No. 31

ABSTRACT

The investigation reported herein concerned the role of imperfections in solids, particularly the interactions between various types of chemical defects and between chemical defects and crystal defects in semiconductors. One part of the study was a theoretical analysis of substituents of Group-IV elements in compounds of elements of Groups III and V. In this work the electrical properties of GaSb with Sn as substituent were calculated from thermodynamic and other considerations. Following this study an experimental program was undertaken to measure the electrical resistivity and Hall effect of GaSb up to nearly 600°C and to infuse small amounts of Sn into GaSb under nearly equilibrium conditions.

Another part of the investigation concerned the diffusion of Pb^{++} ions in single crystal KCl over the temperature range of 200 to 475°C. In this study radioactive tracers were used and the constants for the diffusion equation of Pb in KCl were determined. The results support the theory that diffusion occurs by mobile impurity-vacancy complexes.

Finally, an extensive literature survey of compounds of elements of the I-VII, II-VI, III-V Groups and of the Group IV elements was undertaken and published.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

I INTRODUCTION

This is the Final Report under Contract AF 19(604)-7231 with the
Air Force Cambridge Research Laboratories, on "Investigation of Solid
State Electrolyte Behavior in Semiconductors."

The research chiefly concerned the interactions between various
species of imperfections, both chemical and physical, in crystalline
solids. Such defects and their interactions have previously been treated
as electrolytes in solution in crystalline lattice.[1-11] By adopting
this point of view, it is possible to apply the principle of mass action
to their behavior and thus utilize chemical thermodynamics to understand
their properties. This approach can be applied to any concentration-
dependent imperfection interaction, if sufficiently detailed data are
available on physical properties as a function of concentration of the
imperfection.

Based on this approach a theoretical analysis was made of equilibria
in semiconducting compounds of elements of Groups III and V containing
Group-IV substituents; this work was published as scientific Report No. 1.

Another facet of the research program was an extensive literature
survey covering the physical properties of a wide variety of semicon-
ductors and insulators; the details and mechanics of this work are des-
cribed in the Appendix. The results of the survey were published in
four volumes as Scientific Report No. 2.

An experimental program--largely directed by the theoretical analysis
and by the results of the literature survey--was conducted to extend our
knowledge of solid-state electrolyte behavior. This program consisted
of two phases: One concerned the diffusion of lead in potassium chloride
and the properties of lead-doped potassium chloride; this work was re-
ported in Scientific Report No. 3. The other phase concerned the effect
of the infusion of tin under equilibrium conditions on the properties of
single crystals of gallium antimonide. Discussion of this effort forms
the bulk of the Final Report.

1

Inasmuch as the other portions of the progam have been detailed in Scientific Reports, only summaries will be given in this report. For convenience publications resulting from this investigation are listed below.

Scientific Reports

Scientific Report No. 1, AFCRL No. 62-772, Equilibria in Group III-V Semiconductors Containing Group IV Substituents (36 pages, 4 figures, 4 tables, 40 references)

Scientific Report No. 2, AFCRL No. 26-917(1)
  Vol. I--A Bibliography of Group I-VII Compounds (143 pages)
  Vol. II--A Bibliography of Group II-VI Compounds (120 pages)
  Vol. III--A Bibliography of Group III-V Compounds (64 pages)
  Vol. IV--A Bibliography of Group IV Semiconductors (250 pages)

Scientific Report No. 3, AFCRL No. 63-15, The Diffusion of Lead in Potassium Chloride (42 pages, 13 figures, 3 tables, 21 references)

Papers

A. B. Scott and W. J. Fredericks, Equilibria Among Defects in Group III-V Compounds Containing Group-IV Substituents, to be published in March 1963 issue, Japanese Journal of Applied Physics

F. J. Keneshea and W. J. Fredericks, The Diffusion of Lead in Potassium Chloride, accepted for publication in the Journal of Chemical Physics

Presentations

F. J Keneshea and W. J. Fredericks, The Diffusion of Lead in Potassium Chloride, August 1962 Meeting of the American Physical Society, Seattle, Washington

A. B. Scott and W. J. Fredericks, Equilibria among Defects in Group III-V Compounds Containing Group-IV Substituents, International Conference on Lattice Defects, September 1962, Kyoto, Japan

II THEORETICAL ANALYSIS OF GROUP IV IMPURITIES
IN GROUP III-V COMPOUNDS

The program began with an extensive theoretical analysis of the role and effect of Group-IV impurities in compounds of Groups III and V. The cases of a substituent as an acceptor or a donor, and of pair formation were considered; the general approach was to calculate the free energy difference for substitution of a Group-IV atom in a Group-III and Group-V site. The electrical properties of GaSb with Sn as a substituent were also calculated from thermodynamic considerations. Inasmuch as this analysis was reported in detail in Scientific Report No. 1, only a summary will be presented here.

The analysis treated: first, the distribution of Group-IV impurities on lattices of compounds of the III-V Groups; then, bond energies of compounds of the III-V Groups (and others); and finally, bond energies of Group-IV impurities on various lattice sites. During this treatment estimates of tetrahedral covalent-bond energies for various compounds and Group IV elements were obtained. Table I presents data for 26 crystals of three types, diamond (A4), zinc blende (B3), and wurtzite (B4); Figure 1 presents these data graphically. In these data the single tetrahedral covalent-bond energy for unstrained bonds, $D = \frac{1}{2}\Delta H_S$ for the diamond structure and $\frac{1}{4}\Delta H_S$ for zinc blende and wurtzite structures, where ΔH_S is the molar heat of sublimation, and d is the inter-atomic distance. Finally, estimates of the bond energy of Sn on the GaSb lattice were developed and were found to be, $D_{Sn-Ga} = 33.8$ Kcal/mole and $D_{Sn-Sb} = 32$ Kcal/mole.

The elastic stiffness constants were found to follow "Badger's Rule," as pointed out by Waser and Pauling.[12] For solid elements and some compounds

$$k^{-1/3} = a_{ij}(d - b_{ij}),$$

where a_{ij} and b_{ij} are constants characteristic of the periods containing the two elements joined by the bond of force constant k, and d, as before, is the interatomic distance. For diamond or zinc blende structures,

$$k = a(C_{11} + C_{12}) = 0.679 \frac{d}{A},$$

3

Table I

SINGLE BOND ENERGIES IN CRYSTALS HAVING THE DIAMOND (A4),
ZINC BLENDE (B3), OR WURTZITE (B4) STRUCTURE
(D calculated from data in National Bureau of Standards
Circular 500, U.S. Dept. Commerce, Washington, D.C. (1952),
except as noted; d calculated from L. Pauling, Nature of
the Chemical Bond, 2nd Ed., Cornell Univ. Press, Ithaca
N.Y (1948), p. 179, except as noted)

Number	Formula	Structure	d(A)	$D(\frac{Kcal}{mole})$
1	C	A4	1.54	85
2	Si	A4	2.35	44
3	Ge	A4	2.45	39.2
4	Sn	A4	2.80	35†
5	SiC	††	1.94	71.2
6	ZnO	B3	1.97	43.2
7	ZnS	B3	2.35	33.2
8	ZnSe	B3	2.45	28.4
9	ZnS	B4	2.35	32.4
10	ZnTe	B4	2.63	27.2
11	CdTe	B3	2.80	24.7
12	CdSe	B3	2.62	18.4
13	AgI	B3	2.81	27.6
14	CuCl	B3	2.34	35.7
15	CuBr	B3	2.46	33.6
16	CuI	B3	2.63	30.8
17	AlN	B4	1.96	54.6
18	GaN	B4	1.96	44.3
19	InN	B4	2.14	37.2
20	MgTe	B4	2.76‡	33.4
21	BeO	B3	1.65*	70.3
			1.72**	
22	BeS	B3	2.10	46.4
23	InAs	B3	2.62	32.2‡‡
24	InSb	B3	2.80	30.6‡‡
25	GaSb	B3	2.62	33.0‡‡
26	CdS	B4	2.52	28.7

†ΔH_s from L. Brewer and R. F. Porter, J. Chem. Phys., 21, 2012 (1953)

††Somewhat modified B4

‡Observed (H. Winkler "Stuktur und Eigenschaften der Kristalle,"
2nd Ed. Springer, Berlin (1955), p. 99)

*Calculated from Pauling's radii

**Observed (calculated from data of N. V. Belov and V. I. Mokeeva,
Dokl. Akad. Nauk SSSR, 57, 819 (1947)

‡‡Heat of formation of the compound from W. F. Schottky and M. B.
Bever, Acta Met., 6, 320 (1958)
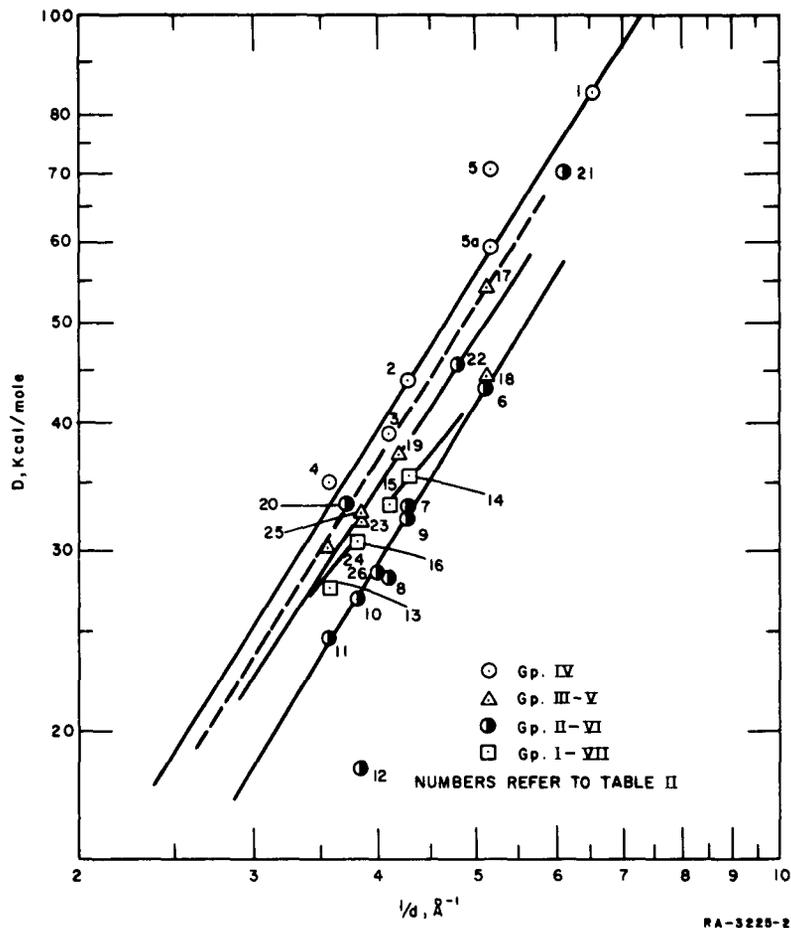
FIG. 1 TETRAHEDRAL COVALENT BOND ENERGIES

where A, the compressibility, is $3/(C_{11} + C_{12})$. The elastic stiffness constants for GaAs,[13] InSb[14], and GaSb[15] are now available. $k^{-1/3}$ for these crystals, and others of the diamond or zinc blende structure for which data are given by Pauling and Waser, is shown as a function of d in Fig. 2, and it is clear that a "Badger's Rule" applies to these crystals as a group. For Group-IV elements, and the III-V compounds a_{ij} and b_{ij} are the same irrespective of period, and the equation is

$$k^{-1/3} = 0.0060(d + 0.92).$$

5
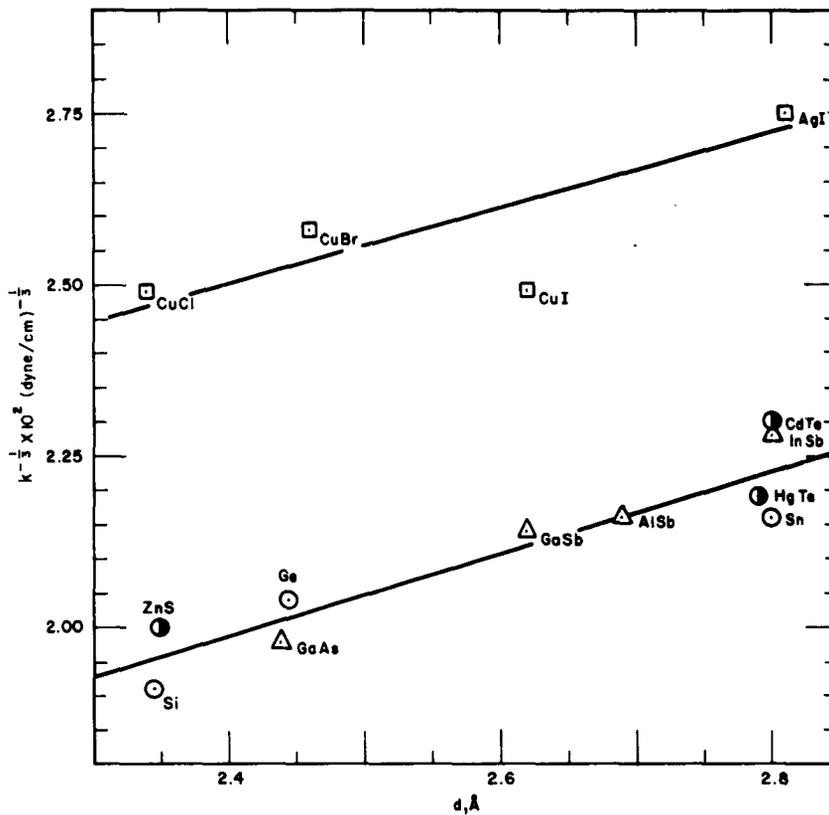
FIG. 2 "BADGER'S RULE" FOR BONDS IN DIAMOND- AND ZINC BLENDE-TYPE CRYSTALS

Here k is in dynes cm^{-1} and d in angstroms. The I-VII compounds fall on a line with a lower slope, thus indicating "softer" bonding.

The next stage in this analysis was the calculation of the free energy required to transfer a Group-IV impurity from one lattice site to another, i.e., the difference in free energy between the two states.

$$\Delta F^{O} = \Delta F^{O}{}_{IV,V} - \Delta F^{O}{}_{IV,III} - T\Delta S^{O}_{c} + 4 \left(D_{IV-III} - D_{IV,V} \right) + \Delta E_{s}$$

where $\Delta F^{O}{}_{IV,V}$ is the free energy of a Group-IV substituent at a Group V site, $\Delta F^{O}{}_{IV,III}$ similarly is a Group-IV substituent at a Group-III site, ΔS^{O}_{c} the crystal entropy, D the bond energies for IV-III and IV-V bonding

6

respectively, and $\triangle E_S$ the strain energy. These calculations are summarized in Table II.

Finally, these data are used to calculate the equilibrium constants for the various imperfection interactions possible in the III-V lattice with a Group-IV substituent. For the case of Sn in GaSb the concentration of various diffusion products in the crystal as a function of the activity of Sn in the external phase in equilibrium with the GaSb crystal (equilibrium constant = K_A) is shown in Fig. 3. The symbols are summarized below

S_1 = concentration of unpaired, nonionized substituent atoms in A sites

S_2 = concentration of unpaired, nonionized substituent atoms in B sites

S_1^+ = concentration of unpaired ionized substituent atoms in A sites

S_2^- = concentration of unpaired ionized substituent atoms in B sites

S_{12} = concentration of ion pairs

p = hole concentration

n = electron concentration

Table II

FREE ENERGY FOR TRANSFER OF SUBSTITUENT FROM B SITE TO A SITE AT 1000°K*

(All energies in Kcal/mole)

Host	$\Delta F^o_{v,B}$	$-\Delta F^o_{v,A}$	$-T\Delta S^o_c$	$4(D_{S-A} - D_{S-B})$				ΔE_S				$\Delta F'^o$			
				Si	Ge	Sn	Pb	Si	Ge	Sn	Pb	Si	Ge	Sn	Pb
AlSb	+27.3	-45.3	+4	+11.6	+ 9.2	+ 7.2	+ 6.8	- 4.7	+5.7	+ 3.0	+ 5.1	- 7	+ 1	- 4	- 2
GaP	+49	-39.9	-2	-16.4	-15.6	-13.2	-12.0	+ 0.7	-2.9	-15.7	-20.1	- 9	-10	-22	-25
GaAs	+24	-39.9	+1	- 7.6	- 8.4	- 5.2	- 5.2	+ 1.6	0.0	- 5.8	- 7.6	-21	-23	-26	-28
GaSb	+27.3	-39.9	+2	+11.6	+ 9.2	+ 7.2	+ 6.8	- 4.3	-3.0	+ 3.0	+ 5.1	- 3	- 4	0	+ 1
InP	+49	-34.4	-3	-32.8	-30.8	-26.8	-24.4	+12.4	+6.2	-16.0	-23.6	- 8	-13	-31	-37
InAs	+24	-34.4	-1	-24.0	-23.6	-1?.8	-17.6	+12.2	+7.8	- 7.8	-13.0	-23	-27	-38	-42
InSb	+27.3	-34.4	+1	- 4.8	- 6.0	- 6.4	- 5.6	+ 5.3	+4.9	0.0	- 1.5	- 6	- 8	-13	-13

*A represents a Group-III atom or lattice site, B represents a Group-V atom or lattice site and S represents a Group-IV substituent atom.
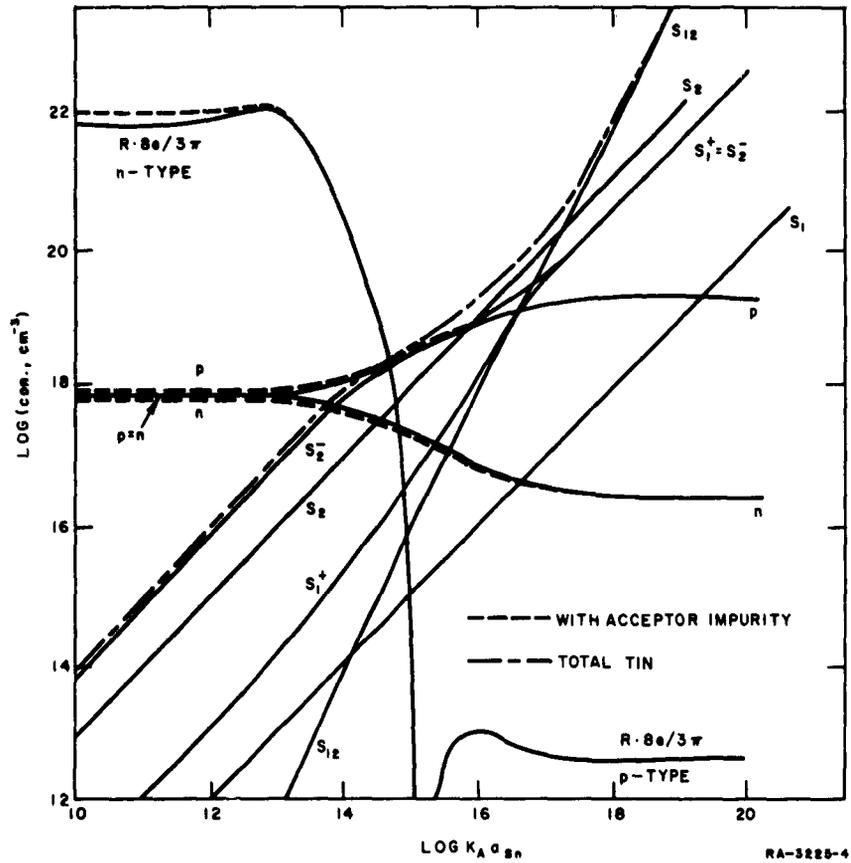
FIG. 3   CONCENTRATIONS OF TIN ATOMS AND IONS AND
CARRIERS, IN GaSb AT 900°K

9

III THE DIFFUSION OF LEAD INTO POTASSIUM CHLORIDE

To explain the relationship between the divalent ion concentration
and the ionic conductivity in potassium chloride, it was postulated that
a complex of a cation vacancy and a substitutional divalent ion was formed.
To confirm the existence of such complexes, experiments were conducted
to determine the diffusion coefficient D as a function of temperature
and concentration. These studies have been reported in detail in Scientific
Report No. 3.

In these studies the diffusion of Pb^{++} ions in single crystal KCl
was studied over the temperature range of 200-475°C. A radioactive tracer
technique was used in two types of measurements: diffusion from a de-
posited surface layer of $PbCl_2$, and diffusion of $PbCl_2$ vapor. A graphical
method has been developed for treating the data from the vapor diffusion
experiments, which enables D to be obtained as a function of Pb concen-
tration. The diffusion of Pb in pure KCl obeys the equation

$$D = 1.02 \times 10^{-3} \exp(-23,300/RT) \, cm^2/sec.$$

The behavior of D as a function of concentration supports the Lidiard[9]
theory of diffusion by mobile impurity-vacancy complexes. In addition,
an association free energy for complex formation has been estimated from
the data to be 0.49 ± 0.1 eV. This is in agreement with the trend shown
in theoretically calculated values for other impurities in KCl. However,
an anomalous rate of diffusion has been observed for Pb near the surface
of some $PbCl_2$-doped DCl crystals.

The confirmation of Lidiard's theories of the concentration dependence
of D is demonstrated in Figs. 4, 5, and 6, reproduced from Scientific
Report No. 3. These data, for three temperatures and several crystal
samples, show excellent agreement with the predicted behavior.
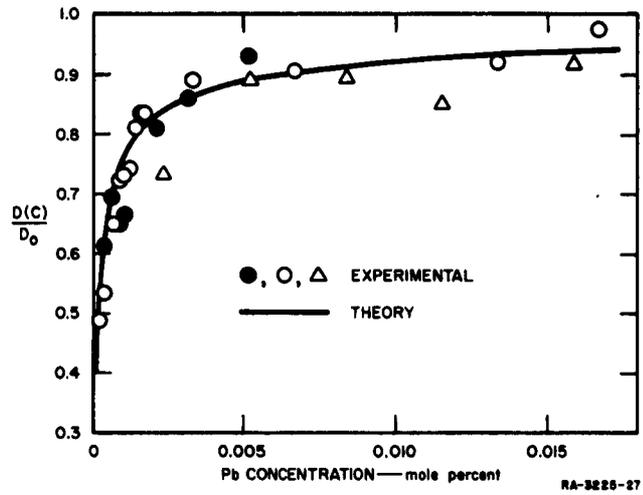
FIG. 4   DIFFUSION OF Pb^{++} IONS IN KCl AS A FUNCTION
OF Pb^{++} CONCENTRATION AT 373°C
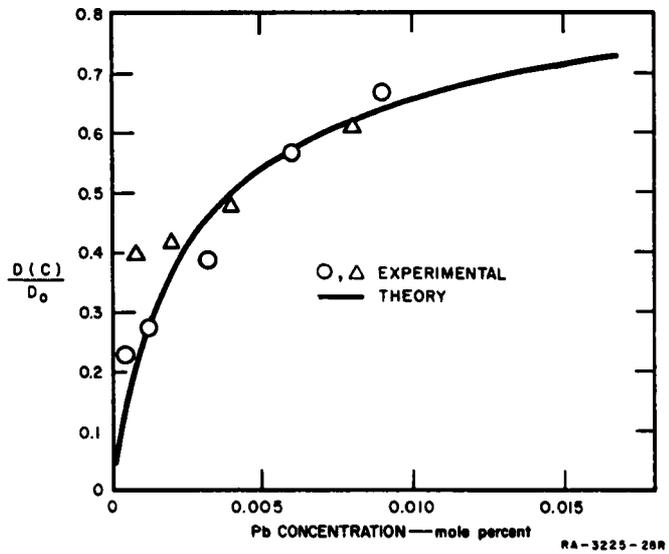
FIG. 5   DIFFUSION OF Pb^{++} IONS IN KCl AS A FUNCTION
OF Pb^{++} CONCENTRATION AT 433°C

11

0.7

0.6

0.5

$\dfrac{D(C)}{D_0}$ 0.4

0.3 O, △ EXPERIMENTAL

0.2 ━━ THEORY

0.1

0

0   0.005   0.010   0.015

Pb CONCENTRATION — mole percent

RA-3225-29R
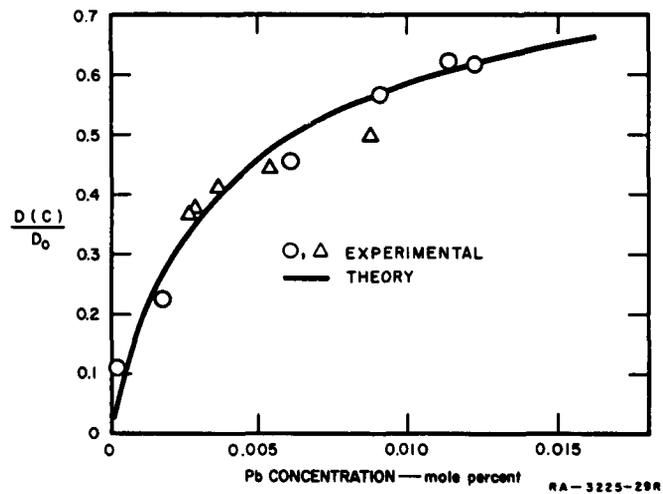
FIG. 6 DIFFUSION OF Pb^{++} IONS IN KCl AS A FUNCTION
OF Pb^{++} CONCENTRATION AT 474°C

IV EXPERIMENTAL INVESTIGATION OF GROUP-IV
SUBSTITUENTS IN GROUP III-V COMPOUNDS

To investigate experimentally the validity of the theoretical calculations summarized in Section II a program was undertaken to diffuse a Group-IV element into a III-V compound under equilibrium conditions, and to measure the effects of such a substituent on the properties of the compound.

GaSb was chosen for the III-V compound because it has a reasonably high melting point and because the onset of intrinsic conduction can be delayed up to about $900^{\circ}K$ by sufficient doping (i.e., by injection of a specific amount of a known impurity). This latter property is desirable so that the effects of impurities will not be masked by the intrinsic conduction. Sn was selected as the Group-IV element because of its low vapor pressure at temperatures of interest and because available thermodynamic data permit calculation of its activity in solutions of possible interest. Furthermore, the small concentrations of Sn required can be measured by the use of radioactive-tracer techniques.

The basic concept of the study required that various measurements (i.e., electrical resistivity and Hall effect) be made before and after doping, and that doping be accomplished under defined conditions, rather than in the poorly defined conditions usually encountered in the incorporation of impurities. Single crystals were necessary in order that the disturbing effects of various crystal orientations and junctures on diffusion rates and equilibrium concentrations would not complicate the problem. As an incidental point, the requirement that electrical measurements be made on the specimens before and after doping implied that soldered contacts could not be used for attaching the necessary contact wires.

Experimental Program

The experimental program thus consisted of (1) injection of Sn into GaSb under conditions which approach equilibrium, and (2) making the required physical measurements over the specified temperature range.

It appeared that the only way in which the Sn could be injected into a specimen of GaSb under controlled conditions was by infusion from a liquid bath in which the concentration and activity of the tin were known. This infusion was to be done, if possible, without changing the shape or structure of the specimen. The major difficulty in achieving this objective was the tendency of the solid specimen to dissolve in the liquid solution containing the tin. Extensive experimentation with a wide range of compositions and temperatures showed that the rate of dissolution of the solid specimen in the liquid was far greater than the infusion rate of the Sn into the solid--often the GaSb specimen would disappear in a matter of minutes.

In making these tests two kinds of evacuated Vycor capsules were used; one had the shape of a figure H, the other was a small bottle. In the H-shaped capsule the cross piece had a bore which permitted the liquid to flow from one leg into the other, but through which the specimen could not pass. Thus, the liquid phase could be poured over the GaSb specimen and then decanted. However, since in all cases the specimen dissolved, decanting was never a problem. In transferring the liquid from one leg to the other the capsule was withdrawn from the furnace, resulting in severe changes in temperature. In order to perform the manipulations isothermally, recourse was made to a small bottle-shaped capsule which could be rotated inside the furnace. A small thermocouple well was inserted longitudinally in the bottle-shaped capsule near the periphery. The specimen rested on this shelf and the liquid phase was rolled on to the specimen at the appropriate temperature. After a certain time the bottle could be rolled in the reverse direction, thereby decanting the liquid from the specimen. Since these operations could be performed in the furnace at temperature with a thermocouple next to the specimen, good control could be maintained.

14

As neither of these methods appeared to offer possibility of use
in a practical system, further attempts along these lines were discontinued.

Theoretical Analysis of Infusion

The only way which appeared to permit the introduction of a small
amount of Sn into the GaSb without losing the GaSb by dissolution involved
the use of a two-phase system, liquid plus solid. In this case, the
equilibrium composition of the solid phase at some particular temperature
would not be far different from that desired in the specimen. To illus-
trate, a portion of a vertical section through the Ga-Sb-Sn ternary
system is sketched below. The section extends from the compound GaSb
toward the Sn corner.
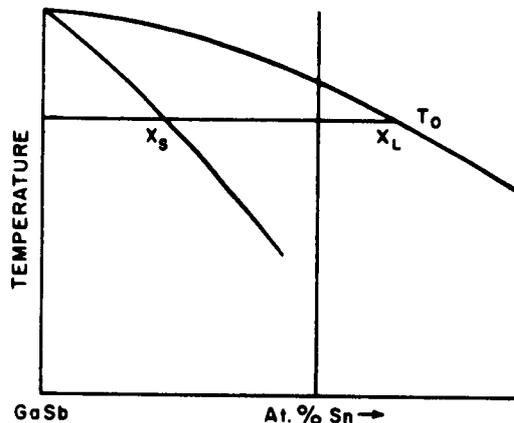
At a temperature, T_o, mixtures whose composition lie between the
liquidus line and solidus line will, in equilibrium, have two phases.
A melt, for example, which has a composition indicated by the vertical
line will have a liquid phase whose composition is given by the inter-
section of the temperature line and the liquidus, and a solid phase
whose composition is given by the intersection of the temperature line
and the solidus. The liquid phase is saturated with respect to the solid
and there is no tendency for the liquid phase to dissolve more of the
solid. Thus it is apparently possible, under these conditions, to insert
a solid specimen into the mixture to absorb some tin, but not to be
dissolved by the liquid phase.

15

In order to explore more carefully this procedure before setting up the rather elaborate experimental apparatus which would be necessary, a theoretical analysis was undertaken. The objectives of the analysis were to determine (1) if the specimen could be expected to survive, and (2) what other changes would occur as the result of the removal of tin from the mixture of liquid plus solid.

The starting point in the analysis was the "lever" relation, which, based on thermodynamic principles, specifies the amount of each phase present under equilibrium conditions. The "lever" relation states that at a given temperature T_O, the amount of liquid phase present is proportional to $x_L/(x_L - x_S)$, while the amount of solid phase present is proportional to $x_S/(x_L - x_S)$, where x_L is the composition of the liquidus, x_S of the solidus, and x of the solution under consideration. If a solid specimen of composition GaSb is introduced into the system represented by the sketch at temperature T_O, the average composition line will move toward a correspondingly lower Sn composition, and the equilibrium amounts of the phases present as described by the lever relation will shift (less liquid and more solid will be indicated).

If in the system of two components A and B, (where A represents GaSb and B represents Sn) we have N gram-atoms of a composition x then the amount of liquid phase at a given temperature is

$$N_L = N\left(\frac{x - x_S}{x_L - x_S}\right)$$

and the amount of solid phase is

$$N_S = N\left(\frac{x_L - x}{x_L - x_S}\right)$$

where N_L is the number of gram-atoms in the liquid phase, N_S is the number in the solid phase, x_L is the atomic fraction of B in the liquid phase, x_S of the solid phase and $N_L + N_S = N$. If now we add a small amount of component A, say n gram-atoms, then the total amount present is N + n grams-atoms, and the composition is x'. We now have for the liquid phase

$$N_L' = (N + n)\left(\frac{x' - x_S}{x_L - x_S}\right)$$

and for the solid phase

$$N_S' = (N + n)\left(\frac{x_L - x'}{x_L - x_S}\right)$$

where $N_L' + N_S' = N + n$.

Furthermore,

$$x = \frac{N_B}{N_A + N_B} \ , \ \text{where } N_A + N_B = N$$

and

$$x' = \frac{N_B'}{N_A + n + N_B} \ , \ \text{and } N' = N_A + N_B + n = N + n,$$

here N_A and N_B are the number of gram-atoms of components A and B present. We have further definitions,

$$N_L = N_{A_L} + N_{B_L}, \quad N_S = N_{A_S} + N_{B_S}$$

$$N_L' = N_{A_L}' + N_{B_L}', \quad N_S' = N_{A_S}' + N_{B_S}'$$

where the superscript indicates the situation after the addition of the solid specimen.

Then

$$x_L = \frac{N_{B_L}}{N_{A_L} + N_{B_L}}, \qquad x_S = \frac{N_{B_S}}{N_{A_S} + N_{B_S}} \ , \ \text{and so forth.}$$

However,

$$x_L = \frac{N_{B_L}}{N_{A_L} + N_{B_L}} = x_L' \quad \frac{N_{B_L}'}{N_{A_L}' + N_{B_L}'}$$

and

$$x_S = \frac{N_{B_S}}{N_{A_S} + N_{B_S}} = \frac{N_{B_S}'}{N_{A_S}' + N_{B_S}'} \ \text{or} \ \frac{N_{B_S}'}{N_S} \ .$$

The points to be resolved concern the relations among N_S, N_S' and n, and specifically to determine if the specimen can be expected to survive. Using the terminology just defined, this requires at least that $N_S' - N_S \geq n$.

Since

$$N_S = N\left(\frac{x_L - x}{x_L - x_S}\right) \text{ and } N_S' = (N + n)\left(\frac{x_L - x'}{x_L - x_S}\right)$$

then

$$N_S' - N_S = (N + n)\left(\frac{x_L - x'}{x_L - x_S}\right) - N\left(\frac{x_L - x}{x_L - x_S}\right)$$

which reduces to

$$N_S' - N_S = \frac{n(x_L - x') + N(x - x')}{x_L - x_S}$$

Using the fact that $N_B = N_B'$, the last equation can be simplified by algebraic manipulation to

$$N_S' - N_S = \frac{nx_L}{x_L - x_S} \ .$$

This equation then gives the difference in the amount of solid phase present before the addition of the small specimen and after the addition.

Another equation of interest concerns the number of B-type atoms in the solid phase. Since

$$N_{B_S}' - N_{B_S} = x_S(N_S' - N_S)$$

then, by manipulation,

$$N_{B_S}' - N_{B_S} = \frac{nx_Sx_L}{x_L - x_S} \ .$$

This then gives the difference in the number of B-type atoms in the solid phase before and after the addition of the specimen.

One last relation of immediate interest is the change in the amount of liquid phase. This works out to be, by similar procedures,

$$N_L - N_L' = \frac{nx_S}{x_L - x_S} \ .$$

18

With these equations we can show what happens when a specimen composed of n gram-atoms of A is inserted in a mixture of liquid and solid phases at equilibrium at temperature T, and the new mixture allowed to come to equilibrium. In an actual infusion run the specimen composition would, however, probably not reach the equilibrium solid composition.

Using the liquidus and solidus curves developed by thermal analysis for GaSb + Sn (to be discussed later) the data in Table III were obtained. The second and third columns give the composition (as the atomic fraction of B) of the liquidus and solidus for a series of decreasing temperatures. The fourth column gives the expected change in the mass of the specimen during the approach to equilibrium. The fifth column gives the change in the number of B (Sn) atoms in the solid phase during the approach to equilibrium. The last column gives the resulting change in the amount of the liquid phase.

Table   III

SOLUBILITY DATA

Temp. (°C)	Atomic Fraction of B in Solidus Composition	Atomic Fraction of B in Liquidus Composition	Change in Solid Phase*	Change in Number of B-Type Atoms in Solid Phase*	Change in Amount of Liquid Phase*
702	.005	.05	1.1n	.005n	- .11n
692	.01	.10	1.1n	.01n	- .11n
667	.05	.20	1.3n	.06n	- .33n
640	.12	.30	1.7n	.20n	- .66n
615	.22	.40	2.2n	.49n	-1.33n

*n = number of gram-atoms in specimen

To clarify the information presented in Table III, consider the data for the highest given temperature, where the composition of the solidus is .005 Sn and that of the liquidus .05 Sn. If a specimen of n-gram atoms is inserted into a melt whose composition is that of the liquidus, the table shows (in the fourth column) not only that the system will not dissolve the specimen but will produce 0.1n gram-atom

more of the solid phase. However, the fifth column indicates that the amount of Sn transferred to the solid phase is only .005n gram-atom and that therefore an additional amount of component A, or GaSb, equal to the difference, will be precipitated. The last column indicates that the decrease in the amount of liquid phase will be equal to 0.11n gram-atom.

In all cases, solid material in addition to the solid specimen is produced; as the atomic fraction of B-type atoms increases, the amount of solid phase precipitated is increased until, as in the higher concentrations of the table, precipitation equal to or greater than the specimen weight results.

There are several conclusions of value which may be drawn from the table. If there is any tendency for the specimen to go into solution followed by a subsequent precipitation (as there conceivably could be, since the free energy of the specimen is higher than that of the equilibrium solid or liquid phase), the liquid surrounding the specimen would become supersaturated with respect to A-type atoms (or, in this case, GaSb) and subsequent precipitation would occur on the specimen itself. On the other hand, if B-type atoms (or Sn) are absorbed by the solid specimen directly from the liquid, the liquid surrounding the solid specimen would become depleted in Sn, tending to make a precipitate form on the solid specimen. Therefore, it is concluded that the result is going to be (1) infusion of tin into the solid specimen, and (2) accretion of solid material on the solid specimen. (Any increase in the size of the specimen will interfere with its insertion into the apparatus, described later on, for making Hall-effect measurements; consequently, any accreted material will have to be removed.)

The reduction in the amount of the liquid phase could have further important consequences. If a technique is used in which the specimen is to be immersed in a suitable liquid by pouring the liquid onto the specimen, followed by decanting some time later, the chief difficulty will be the resistance to flow of the slurry of the solid and liquid phases. The

fact that any reduction in tin in the liquid phase will result in an increase in the amount of solid phase, which may or may not form on the specimen, will make still more difficult such a technique.

Thermal Analysis

In the preceding discussion it was pointed out that the only apparently feasible way to introduce the tin into the solid GaSb was through the insertion of the specimen into solutions of GaSb + Sn which existed in equilibrium in two-phases, liquid plus solid, by selection of the appropriate temperature-composition relationships. In order to accomplish this, it was necessary to determine by thermal analyses the liquidus, and solidus if possible, near the compound GaSb in the vertical section of the ternary diagram joining the compound GaSb and Sn.

The thermal analyses were made on alloys melted in Vycor capsules under vacuum and sealed. The materials used were reagent grade or better (99.9% purity). In general the Vycor capsules had the configuration (shown in Fig. 7) which permitted measurements on three different compositions in each sealed capsule. The first composition was placed in the leg with the thermocouple well and successive additions of Sn (with the capsule at about 400°C) could be made by pouring the Sn from each leg into the measurement leg. This arrangement was possible because the vapor pressure of all the components is low and no mixing occurred due to transfer through the vapor phase. It had the advantage of using very little gallium, since the charges weighed on the order of 5 grams, of which only a gram or so was gallium.

The thermal analyses were mainly confined to cooling curves and these were plotted on a Mosely X-Y recorder; some sample cooling curves are shown in Fig. 8. In this case elapsed time is plotted on the X-axis at a rate of about 1 inch per minute. The scale of the Y-axis is 1 inch per millivolt and, with the chromel-alumel thermocouples used this results in a temperature scale of approximately 24°C per inch at temperatures of interest. The results were reproducible to ± 2.5° of the mean
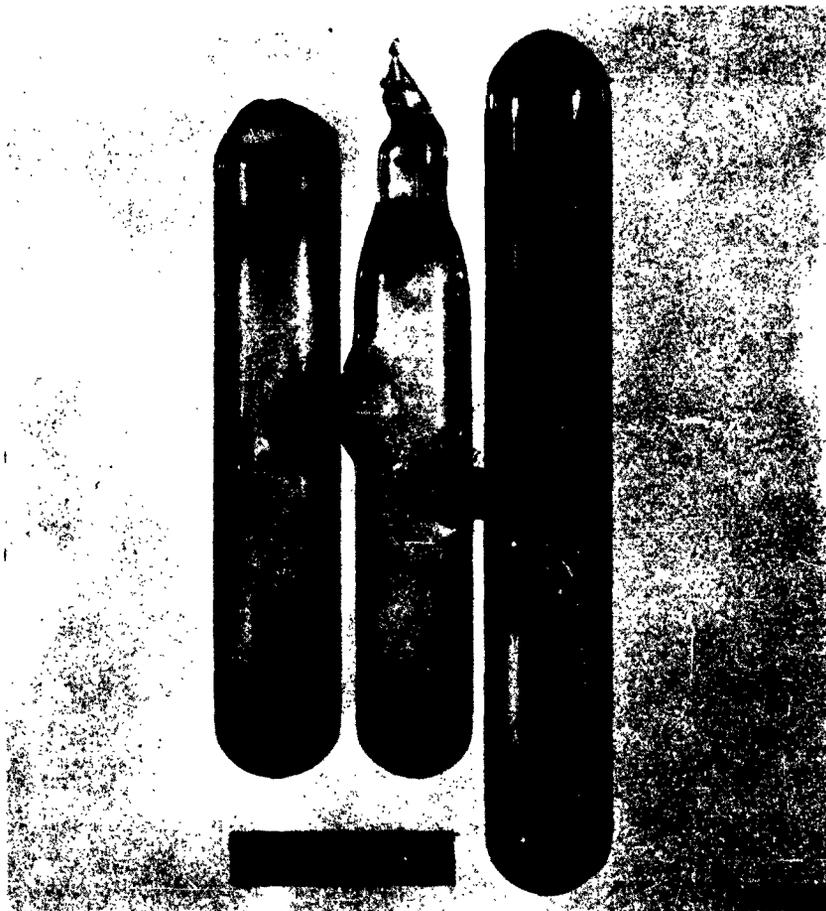
FIG. 7   VYCOR THERMAL-ANALYSIS CAPSULE
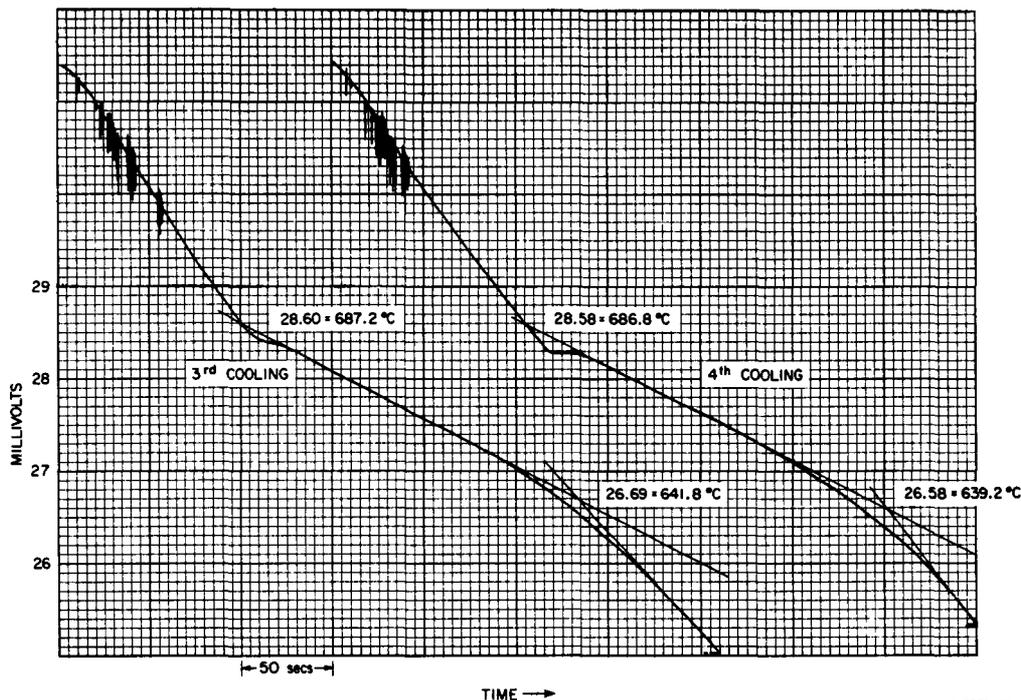
FIG. 8   COOLING CURVE FOR GaSb + 11.1 AT 0% Sn

temperature for liquidus temperatures at low Sn contents ($<$ 30 at. $\%$).
Solidus temperatures were, as expected, less reproducible, and of
course, due to nonequilibrium cooling conditions, less accurate.   For
the compositions which had 30 at. $\%$ or more Sn, the spread of apparent
liquidus temperatures increased to around $10°$ ($\pm5°$ around the mean) or
more.   Further, there seemed to be a drift toward higher indicated
temperatures as the number of runs increased.   Both the spread and
drift were inexplainable, but it was conjectured that there might be
a reaction with the Vycor container at the higher Sn concentrations,
and consequently diffusion runs were held to Sn concentrations of 25
at. $\%$ or less.

23

Table IV shows the results of these experiments and Fig. 9 shows the pertinent portion of the GaSb-Sn vertical section of the ternary system. There are two conclusions which should be noted. The first is that the apparent solubility of Sn in solid GaSb is quite large, much larger than the 0.5 at. % solubility reported for Sn in GaAs.[16] The second conclusion is that Sn replaces the Ga and Sb atoms in equal proportions when it enters the GaSb lattice. While neither of these conclusions can be considered as certain on the basis of these data, they do appear reasonable. The reasoning which leads to these conclusions is as follows.

Table IV

RESULTS OF THERMAL ANALYSIS ON GaSb PLUS Sn

Composition at. % Sn	Liquidus Temp., °C	Solidus Temp., °C
(GaSb)	706	
5.13	703 ± 1.5	662 ± 1.5
8.12	697 ± 2.0	655 ± 2.2
11.1	686 ± 1.6	643 ± 9.0
14.2	682 ± 1.3	643 ± 2.5
20.0	667 ± 2.3	619 ± 3.3
30.0	641 ± 5.0	597 ± 8.5
40.0	619 ± 4.5	547 ± 10.3
50.0	595 ± 12.0	512 ± 5.0

The thermal analysis data portrayed in Fig. 8 indicate no reactions on cooling beyond the process of solidification through a two-phase field. If this is all that occurs, then the solid just below the solidus line must have the same composition as the liquid above the liquidus, and therefore there must be a large solubility of Sn in the GaSb lattice. At lower temperatures the solubility limit of Sn will no doubt decrease, but this cannot be investigated easily by thermal analysis.
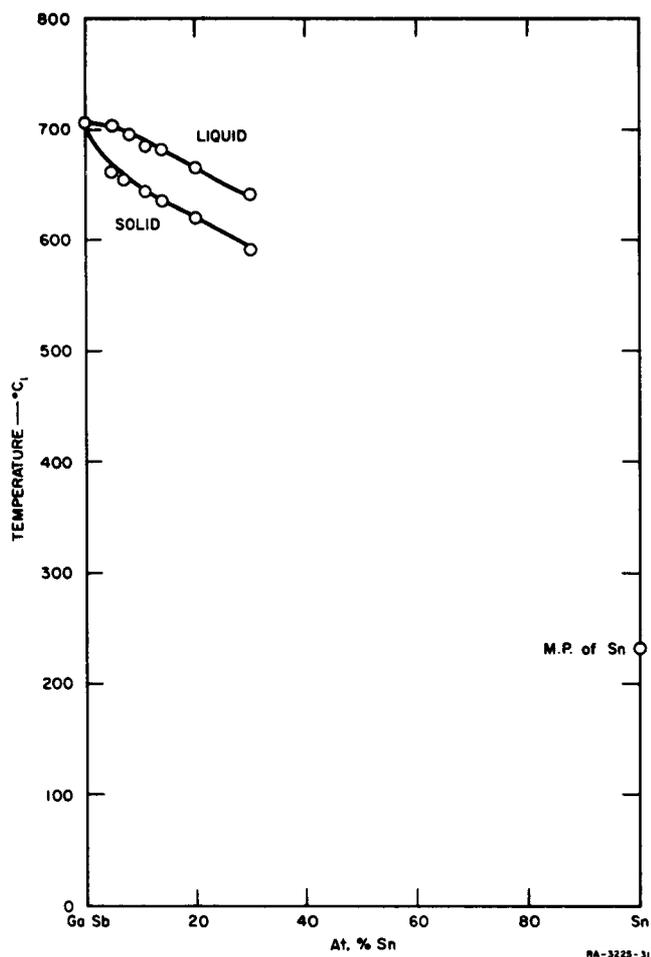
FIG. 9   RESULTS OF THERMAL ANALYSIS ON GaSb + Sn

Study of the three binary constitution diagrams, which have all been delineated, with reference to possible configurations of the ternary constitution diagram, which has not been delineated, leads to at least two reasonable constructions for the phases on the basal plane. These are shown in Fig. 10. The one on the bottom, in addition to the two-phase field GaSb + SbSn, shows a two-phase field, GaSb + Sn. These diagrams neglect the existence of the crystal transformation in Sn at $13^{\circ}C$ by assuming that the low temperature phase does not affect the horizontal, isothermal planes, above this temperature. However

25
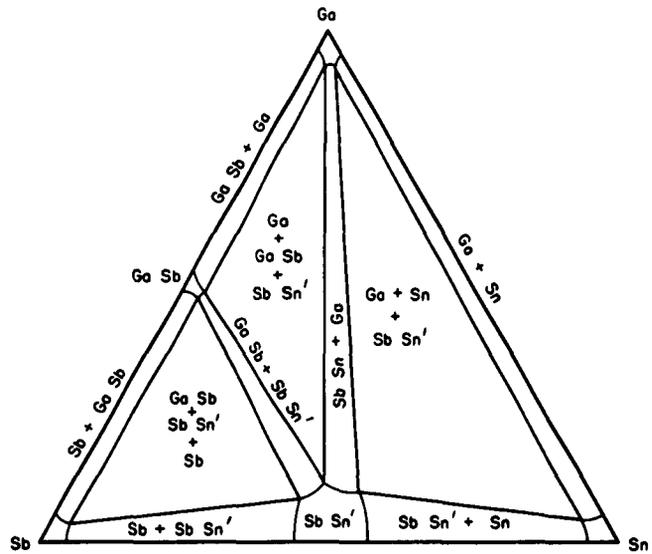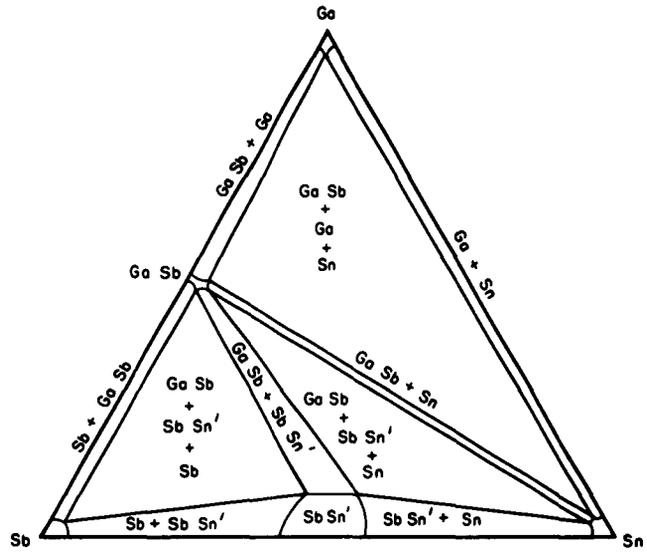
FIG. 10 BASAL-PLANE CONSTRUCTIONS OF Ga-Sb-Sn SYSTEM

26

the similarity of the crystal structures of the low temperature form of Sn (cubic, a = 6.491 A) and of GaSb (cubic, a = 6.105 A) could result in a complete series of solid solutions between the two components.

The diagram on the bottom leads to a vertical section through GaSb + Sn which is not substantiated by the thermal analysis, while the diagram on the top leads to a vertical section which is at least compatible with the thermal analysis. While there certainly is some ambiguity in these conclusions, the diagram on the top is considered to be the more likely of the two. In addition, it may be concluded that the solubility of Sn in GaSb is, at least at some temperatures, quite large.

If the solubility of Sn in GaSb is reasonably large, then it may be further surmised that Sn replaces the Ga and Sb atoms in equal numbers. This conclusion is reached because the solubility of both Ga and Sb in GaSb is shown by the work in the binary system to be vanishingly small, and therefore the solid field, GaSb + Sn, must extend in a narrow field into the ternary system toward the Sn corner. If this is correct, then the Sn atoms must replace the Ga and Sb atoms in equal numbers. There is, however, the fact that the side of the single-phase field GaSb containing Sn abuts the two-phase field GaSb + SbSn, and this could indicate that with the addition of Sn the GaSb structure could be at least somewhat receptive to excess Sb atoms.

Measurement of Hall Effect and Electrical Resistance

In order to determine the number and type of the carriers of electrical charge, the Hall voltage and the electrical resistivity were measured. These measurements had to be performed on single crystals of the GaSb over a wide range of temperatures before and after injection of small amounts of Sn. These requirements indicated (1) that fairly large (and thick) specimens had to be used, (2) that welded contacts could not be used because of contamination during the subsequent diffusion treatment, and (3) that single crystals had to be used in order to avoid diffusion along grain boundaries which would result in nonuniform tin concentrations.

For making measurements at room temperature and below, the device shown in Fig. 11 was designed and constructed. The specimen rested in a close-fitting bed in the center of the specimen holder. Since the GaSb single crystals were irregular in shape but nominally of the same width, the device was constructed to accept specimens of varying lengths and thicknesses. The close-fitting bed supported the specimens and reduced the tendency to fracture because of pressure from the side contacts.
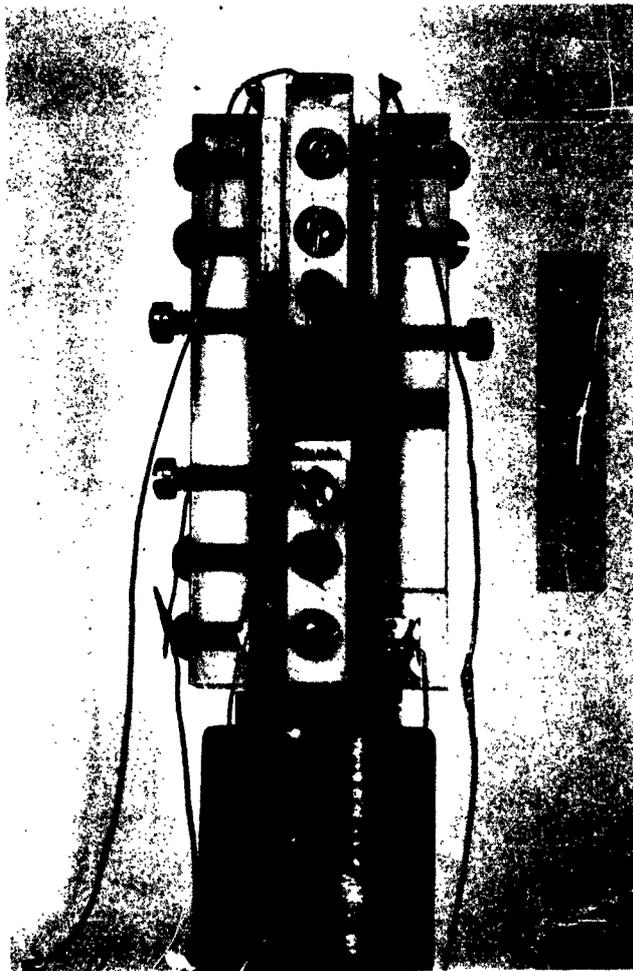

FIG. 11   SPECIMEN HOLDER FOR LOW TEMPERATURE HALL MEASUREMENTS

The specimen holder itself was made of Lucite, while the contacts were made of beryllium-containing copper and the other metal parts were of brass. Use of this device presented no unusual problems. The critical question concerning the use of the device was whether or not satisfactory electrical contact could be made and maintained at all temperatures with the spring contacts; after the contact faces had been polished fairly flat, no further difficulties were experienced.

For measuring the Hall voltage and the electrical resistivity from room temperature up to 500 or 600°C a different apparatus had to be built. This apparatus was essentially the same as that for the low temperature measurements with appropriate changes in materials for the higher temperatures.

Figure 12 shows an over-all view of the apparatus with the specimen holder in the center between the magnet poles. The space inside the Vycor or glass tube is evacuated to cut down heat losses and to protect the specimen and the molybdenum metal parts.

Figure 13 shows a detailed drawing of the specimen holder. The base is made of boron nitride with a heater coil wound around the outside. The coil itself is wound noninductively in order not to affect the magnetic field which is applied to the specimen.

All the metallic parts are made of molybdenum, except for the heating coil which is wound of constantan wire. A copper-constantan thermocouple is inserted into the boron nitride body and rests not more than 1/8 inch from the specimen. All the lead-in wires (except the thermocouple and the heater-coil power leads) are molybdenum so that no thermoelectric voltages are generated in the lead-in wires.

The chief difficulties with the use of the high temperature device resulted from arcing between the posts used for tying down the lead-in wires to the heater coil. This arcing occurred at the heater voltages required for the higher temperatures whenever a large abrupt change in the magnetic field strength was made. Consequently, at the higher

4" dia. "O" RING

VYCOR TUBE — 2" O.D.
2.5 mm. WALL

HEATER LEAD-IN
WIRES

$\frac{3}{4}$" STAINLESS STEEL
TUBE

$11\frac{3}{4}$"

POLE

POLE

SPECIMEN
HOLDER

HALF SCALE

2 1/4" dia "O" RING

PLATE INTO WHICH
TUBING IS SOLDERED

TO VACUUM
PUMP

STEEL
BRASS
VYCOR
MOLYBDENUM
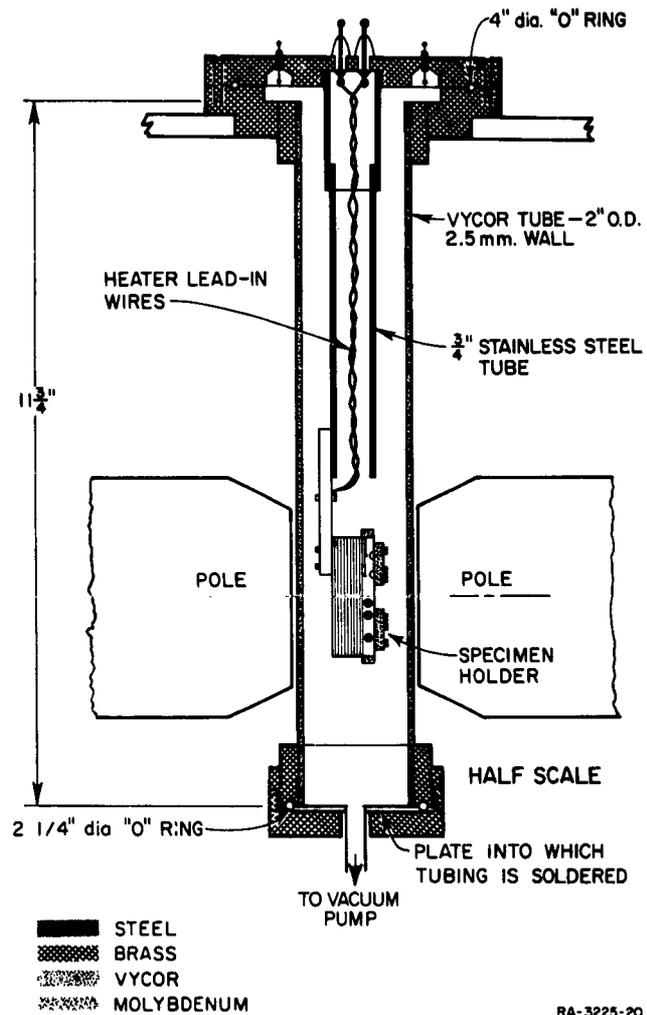
RA-3225-20

FIG. 12 APPARATUS FOR MAKING HIGH TEMPERATURE HALL MEASUREMENTS

TOP VIEW SHOWING
ARRANGEMENT OF
GROOVES

PIN

IO GROOVES TO RECEIVE
0.012" WIRE. HEATER
ELEMENT~60 inches
NO. 30 OR NO. 28 BARE
CONSTANTAN WIRE. (OR
Nb OR Ta)

A

PIN TO ANCHOR COIL

SPECIMEN

VYCOR TUBE
(2" O.D.)

A

FRONT VIEW

SIDE VIEW

SPECIMEN

$\frac{1}{8}$"THERMOCOUPLE WELL

BORON NITRIDE

MOLYBDENUM

SECTION THRU AA

RB-3225-19
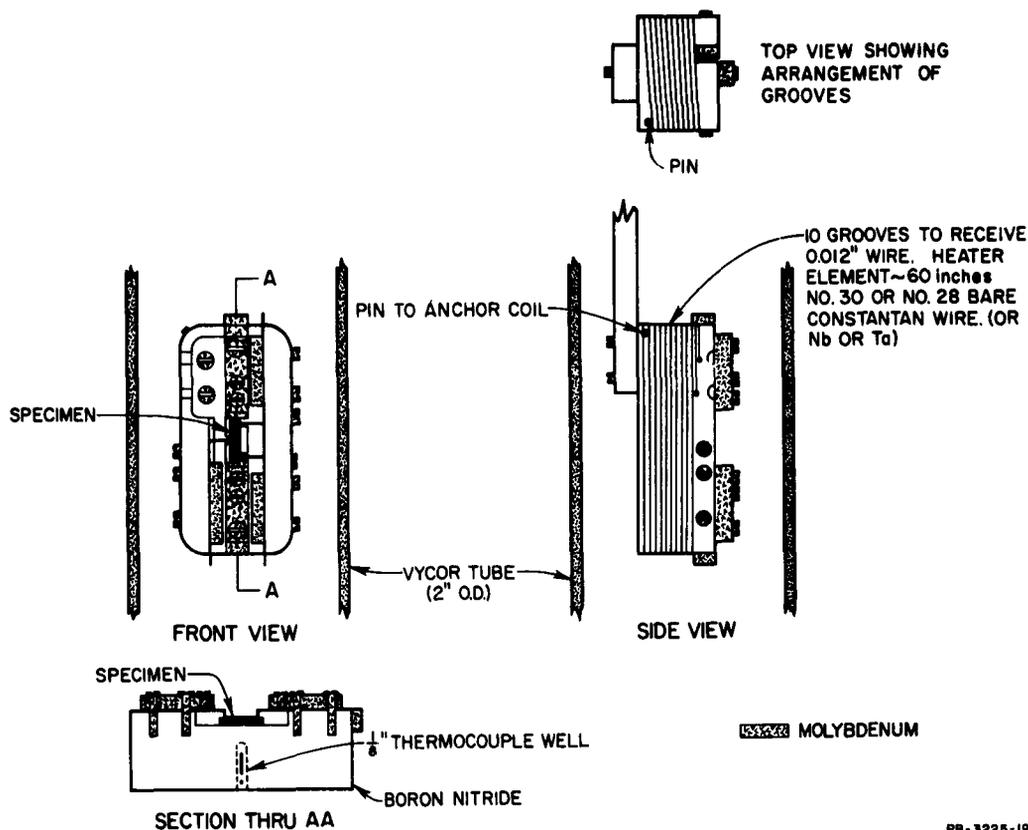
FIG. 13   SPECIMEN HOLDER FOR HIGH TEMPERATURE HALL MEASUREMENTS

temperatures not more than about 5-kilogauss field strengths were possible, in spite of improvement in the vacuum during the course of the experiments.

The results of the measurements of resistivity and Hall effect are shown in Fig.s 14 and 15. The chief feature of interest is the reversal of sign of the Hall coefficient at about 310°C; this compares closely with previous measurements, as for example, that of Leifer and Dunlap[17] of 357°C. The GaSb used in these particular measurements was obtained from A. D. Mackay Inc. in the form of small slabs about 1 mm thick cut from a single crystal about 0.8 cm in dia. The specimens exhibited p-type con-duction, as have all essentially pure GaSb samples for which measurements have been reported in the literature. The electrical resistivity of these specimens was also comparable to resistivities reported in the literature for other specimens.

31
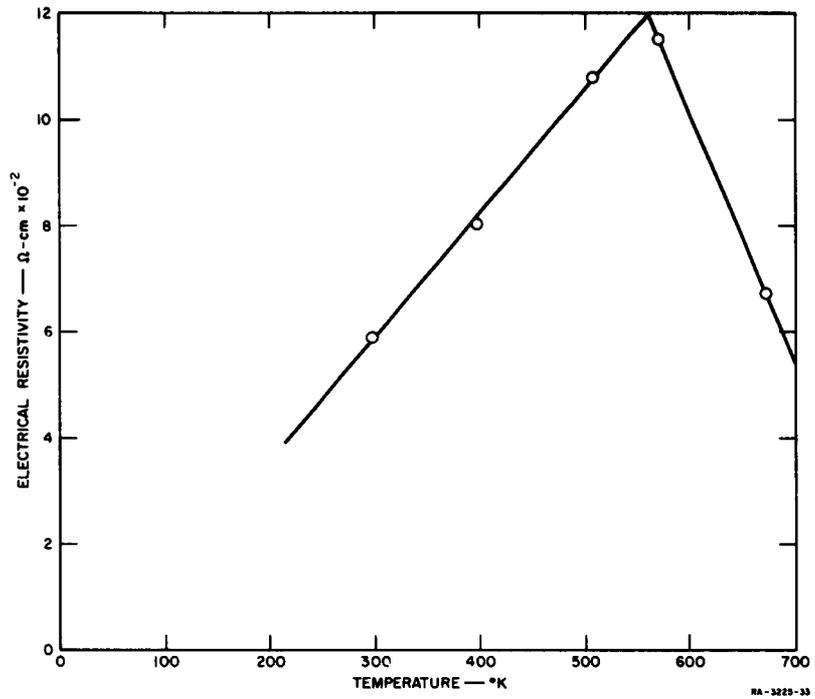
FIG. 14   HALL EFFECT vs. TEMPERATURE FOR GaSb
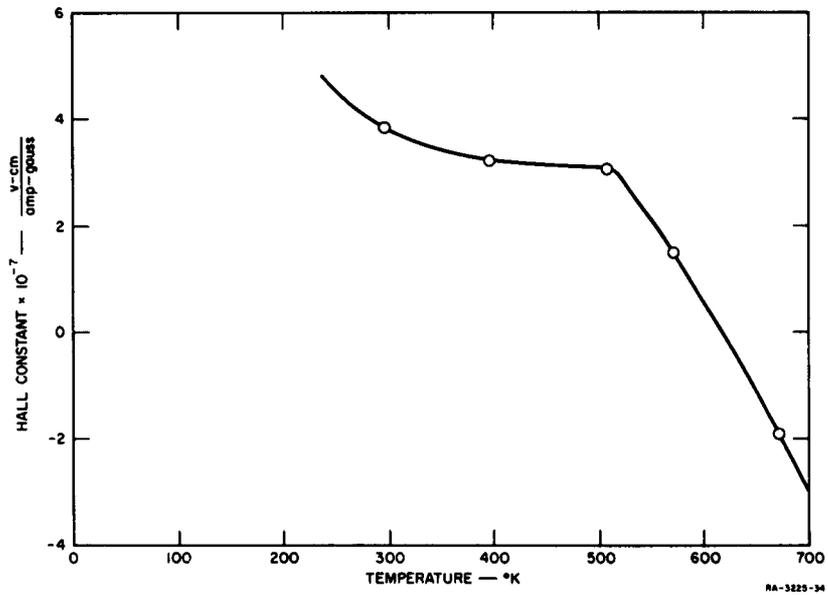
FIG. 15   ELECTRICAL RESISTIVITY vs. TEMPERATURE FOR GaSb

V SUMMARY

This investigation of solid state electrolytes produced the following results: First, a comprehensive survey of the literature on the more important electronically active compounds and elements was compiled. The four-volumes (Scientific Report No. 2) resulting from this effort should be of major importance to workers in this field. Second, the behavior of Group-IV substituents in III-V compounds was analyzed for the case of equilibrium of the Group-IV element between the crystal and the external phase. Third, a method to test experimentally these calculations was developed, although time did not permit completion of the experimental test. Four, the energy of association for a cation vacancy with Pb^{++} in KCl was determined. Five. the energy for thermal migration of Pb^{++} in KCl was measured. Six, the concentration dependence of the diffusion constant was determined and Lidiard's theory for its behavior verified. An attempt to measure the effect of an external electrical field on the diffusion of Pb^{++} in KCl was initiated but was not completed. All completed phases of this program have been reported in detail in Scientific Reports and many of the results have been submitted to the literature.

D. S. Bloom, Chairman
Solid State Department

DSB:blm

REFERNECES

1. C. Wagner and W. Schottky, Z. physik. Chem. B11, 163 (1931)

2. C. Wagner, Z. physik. Chem. Bodenstein Festband, p. 177 (1931)

3. C. Wagner, Z. physik. Chem. B22, 181 (1933)

4. C. Wagner, Z. Elektrochem. 39, 543 (1933)

5. W. Schottky, Z. physik. Chem. B29, 335 (1935)

6. W. Schottky, Z. Elektrochem. 45, 33 (1939)

7. W. Schottky, Halbleiterprobleme I (W. Schottky, ed.) Vieweg, Braunschweig, 1954, p. 139

8. F. A Korger and H. J. Vink, Solid State Physics Vol. 3, F. Seitz and D. Turnbull eds., Academic Press, New York, 1956, p. 307

9. A. B. Lidiard, Handbuch Der Physik Band XX, S. Flugge ed., Springer-Verlag, Berlin, 1957, p. 246

10. H. Reiss, C. S. Fuller and F. J. Morin, Bell Syst. Techn. J., 35, 535 (1956)

11. F. Seitz, Imperfections in Nearly Perfect Crystals, W. Shockley, ed., Wiley, New York, 1952, p. 3

12. J. Waser and L. Pauling, J. Chem. Phys. 18, 747 (1950)

13. T. B. Bateman, H. J. McSkimino and J M. Whelan, J. Appl. Phys. 30, 544 (1959)

14. R. F. Potter, Bull. Am. Phys. Soc. Ser. II, 1, 53 (1956)

15. H. J. McSkimio, W. L. Bond, G. L. Pearson and H. J. Hrostowki, Bull. Am. Phys. Soc. Ser. II, 1, 111 (1956)

16. C. Kolm, S. A. Kulin and B. L. Averbach, Phys. Rev. 108, 965 (1957)

17. H. N. Leifer and W. C. Dunlap, Phys. Rev. 95, 51 (1954)

Appendix

LITERATURE SURVEY

Appendix

LITERATURE SURVEY

The purpose of this Literature Survey was to produce a set of
abstracts which would be of use to persons working in solid-state physics,
especially solid-state electrolyte theory.

For this program it was necessary to be able to select abstracts by
composition, property or phenomena, general material class, and author.
In any Keysort system a compromise must be reached between an unambiguous
coding system and an easily usable system within the limitation of coding
symbols available. A coding system similar to that used in Beilstein
or in the International Critical Tables could be devised. However, this
would involve first coding the elements by number--their atomic number
would be natural; then coding each compound, considering each compound
in terms of the ascending atomic number of each constituent element.
Thus, the problem is to code numbers between 0 1 and 0 9 for each element
in the compound, and a second number from 1 to 14 for the quantity of
each element. The usual number coding system for 1 to 99 in McBee cards
requires 5 double holes for each number between 0 and 9 (the same five
will produce any number between 0 and 14 inclusive). Each element would
require 15 double holes and, if ternary compounds are to be considered
the most complicated compounds of interest, 45 double holes must be
reserved for them. This system makes no allowance for indexing impurities.
To select a particular ternary compound in which the atomic number of
each element is greater than 9 would require 18 selection operations,
i.e., 6 for each constituent element. It soon becomes apparent that
although this system has very little ambiguity in compound selection,
its symbol requirement is large and the number of operations necessary
to isolate a particular compound is a maximum of six times the number of
elements in the compound--obviously not a satisfactory system for a hand-
sorted index. It does not offer use in machine-sorted index systems having
greater symbol capacity.

It was decided to use a simpler system with more direct coding, fewer operations for compound selection, more economical use of card symbols, and a method for inclusion of impurity data. However, the price of these gains was to introduce slightly more ambiguity into the selection of compounds. The system used requires 29 double holes. The general scheme is to place a ? ng-form periodic table of the elements in the upper right-hand corner of the card. This requires 18 code symbols across and 8 down. The Rare Earth group uses the last horizontal row. The elements of which the compound is composed are punched in the deeper of the corresponding symbols. Thus two operations are required to select each element in the compound, one for the period and one for the group. Then to distinguish between compounds which are composed of the same elements but with different composition ratios, three double holes are used to code numbers between 2 and 8, which correspond to the total number of atoms per molecule.

Impurity elements can be indicated by punching only the shallow hole in th s element-coding system. The cards containing compounds of the impurity el ment, as well as those in which it is an impurity constituent, will be separated on the first selection; then the compounds can be separated from the impurity cards by the same code, but by the deep rather than the shallow hole.

Certain ambiguities can arise in this system. Compounds which are composed of the same elements with the same total number of atoms per molecule cannot be separated. This is a relatively rare occurrence. A more frequent case of ambiguous selection occurs when more than one compound is discussed in a single abstract and both compounds are coded on a single card. In most cases of this type a second card has been used which refers to the main card; however, when both compounds can be coded on the same card unambiguously this is done.

The index for author coding is shown in Table A-1. This index is based on a name-occurrence-frequency numerical code developed by the McBee Company.* This system does not permit more than one author to be indexed per card. In general only the first author has been indexed.

---

*I. A. Breger, Economic Geology 53, 325 (1958)

Aa to Al	01	Haa to Hak	35	Pa to Pd	67
Am to Aq	02	Hal to Haq	36	Pe to Pg	68
Ar to Az	03	Har to Hd	37	Ph to Pz	69
		Hea to Hem	38		
Baa to Baq	04	Hen to Hh	39	Qa to Qz	70
Bar to Bd	05	Hi to Hn	40		
Bea to Bem	06	Ho to Ht	41	Ra to Rd	71
Ben to Bh	07	Hu to Hz	42	Re to Rh	72
Bi to Bn	08			Ri to Rn	73
Bo to Bq	09	I to Iz	43	Ro to Rt	74
Bra to Brn	10			Ru to Rz	75
Bro to Bt	11	Ja to Jn	44		
Bu to Bz	12	Jo to Jz	45	Sa to Sch	76
				Scha to Schl	77
Caa to Car	13	Ka to Kd	46	Schm to Scht	78
Cas to Cg	14	Ke to Kh	47	Schu to Sd	79
Ch to Chz	15	Ki to Km	48	Se to Sg	80
Ci to Cu	16	Kn to Kq	49	Sh to Shz	81
Coa to Coq	17	Kr to Kz	50	Sı to Sl	82
Cor to Cq	18			Sm to Sn	83
Cr to Cz	19	La to Ld	51	So to Sr	84
		Le to Lh	52	Sta to Std	85
Da to Dd	20	Li to Ln	53	Ste to Stm	86
De to Dh	21	Lo to Lz	54	Sto to Stz	87
Di to Dq	22			Su to Sz	88
Dr to Dz	23	Maa to Maq	55		
		Mar to Mb	56	Ta to Tg	89
Ea to El	24	McA to McF	57	Th to Tn	90
Em to Ez	25	McG to Md	58	To to Tz	91
		Mea to Meq	59		
Fa to Fh	26	Mer to Mh	60	Ua to Uz	92
Fi to Fk	27	Mi to Mn	61		
Fl to Fq	28	Mo to Mt	62	Va to Vz	93
Fr to Fz	29	Mu to Mz	63		
				Wa to Wd	94
Ga to Gd	30	Na to Nh	64	Wea to Weh	95
Ge to Gk	31	Ni to Nz	65	Wei to Wg	96
Gl to Gq	32			Wh to Wilk	97
Gra to Grk	33	Oa to Oz	66	Will to Wz	98
Gri to Gz	34				
				Xyz	99

The subject index is the simple assignment of a particular symbol to a general phenomenon or property, each of which can be further divided into 14 subclasses. The detailed indexing of subclasses has not been attempted as yet. In the process of classification it has been found that very seldom do more than three general subject classes occur on any single card. Therefore three groups of five double symbols have been tentatively reserved for detailed subclass indexing. In addition, the general subject index separates review papers by punching both symbol holes, while other papers are only punched a single hole.

Finally, a general compound classification index has been included. This index sorts materials according to type of chemical bonding--i.e., ionic, homopolar, metallic. It also separates the alkali halides from other ionic compounds; compound semiconductors from elemental semi-conductors; and metals and alloys from intermetallic compounds. Some ambiguity may arise because of differences among various researchers in classifying compounds.

A coding card is shown in Fig. A-1. It was not found necessary to code the detail subject index. During the course of the survey it was found necessary to broaden some classifications, for example "thermoelect' includes thermal conductivity data also.

FIG. A-1 CODING CARD FOR LITERATURE SURVEY

Deep Punch Major
Shallow Punch Impurity

		I	II	III	IV	V	VI	VII	VIII			I	II	III	IV	V	VI	VII	0
		H																	He
		Li	Be									B	C	N	O	F	Ne		
		Na	Mg									Al	Si	P	S	Cl	Ar		
		K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	K
		Rb	Sr	Y	Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
		Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
		Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf						
		Ce	Pr	Nd	–	Sm	Eu	Gd	Td	Dy	Ho	Er	Tm	Yb	Lu				

No. Atoms per Molecule
2 } Two
3 } Deep
4
3+2 } One
4+2 } Deep
3+4
4+4

Numerical Code 01 to 99
Author McBee

* Main Card is Basic Card for Series Cross Filed

General Material Types:
138 — Intermetallic – Metal (A)
137 — Alkali Halides – Ionic (B)
136 — Elemental Homopolar – Homopolar (D)
135 — Elemental Semicond. – Semicond (G)

Theory
Lattice Dynam.
Surfaces
Imperfections
Electronic Cond. and Hall Coeff.
Ionic Cond.
Photocond. and Photoelect.
Thermoelect. and Therm. Cond.
Dielectric
Diffusion
Optical Theory
Optical Absorption
Reflection Spectra
Luminescence
Suscept (NMR–EPR)
Thermionic Emiss.
Thermodynamics
Mechanical
Struture

Deep Punch Subject Index for Review Papers
Crystal Growth
Material Preparation

SUBJECT
MAIN
MAIN SUBJECT
* PUNCH IF MAIN CARD

UNITS

40

AF Cambridge Research Laboratories, Bedford, Mass. "Investigation of Solid-State Electrolyte Behavior in Semiconductors," by W. J. Fredericks, F. J. Keneshea, D. S. Bloom, A. B. Scott. February 1963, 44 pp. incl. 16 illus. AFCRL-63-74 Unclassified Report

This report covers an investigation into the role of imperfections in solids, particularly the interactions between various types of chemical defects and between chemical defects and crystal defects in semiconductors. One part of the study was a theoretical analysis of substituents of Group-IV elements in compounds of elements of Groups III and V. In this work the electrical properties of $GaSb$ with Sn as a substituent were calculated. Another part of the study was an experimental program to measure the electrical resistivity and Hall effect of $GaSb$ up to nearly 600°C and to infuse small amounts of Sn into $GaSb$ under nearly equilibrium conditions.

AF Cambridge Research Laboratories, Bedford, Mass. "Investigation of Solid-State Electrolyte Behavior in Semiconductors," by W. J. Fredericks, F. J. Keneshea, D. S. Bloom, A. B. Scott. February 1963, 44 pp. incl. 16 illus. AFCRL-63-74 Unclassified Report

This report covers an investigation into the role of imperfections in solids, particularly the interactions between various types of chemical defects and between chemical defects and crystal defects in semiconductors. One part of the study was a theoretical analysis of substituents of Group-IV elements in compounds of elements of Groups III and V. In this work the electrical properties of $GaSb$ with Sn as a substituent were calculated. Another part of the study was an experimental program to measure the electrical resistivity and Hall effect of $GaSb$ up to nearly 600°C and to infuse small amounts of Sn into $GaSb$ under nearly equilibrium conditions.

UNCLASSIFIED

An investigation also was conducted using radio-
activity tracers on the diffusion Pb^{++} ions in
single crystals of KCl over a temperature range
of 200 to 475°C and the constants for the dif-
fusion equations of Pb in KCl were determined.
These results support the theory that diffusion
occurs by mobile impurity-vacancy complexes.

UNCLASSIFIED

An investigation also was conducted using radio-
activity tracers on the diffusion Pb^{++} ions in
single crystals of KCl over a temperature range
of 200 to 475°C over the constants for the dif-
fusion equation of Pb in KCl were determined.
These results support the theory that diffusion
occurs by mobile impurity-vacancy complexes.

UNCLASSIFIED

An investigation also was conducted using radio-
activity tracers on the diffusion Pb^{++} ions in
single crystals of KCl over a temperature range
of 200 to 475°C and the constants for the dif-
fusion equation of Pb in KCl were determined.
These results support the theory that diffusion
occurs by mobile impurity-vacancy complexes.

UNCLASSIFIED

An investigation also was conducted using radio-
activity tracers on the diffusion Pb^{++} ions in
single crystals of KCl over a temperature range
of 200 to 475°C and the constants for the dif-
fusion equation of Pb in KCl were determined.
These results support the theory that diffusion
occurs by mobile impurity-vacancy complexes.

STANFORD
RESEARCH
INSTITUTE

MENLO PARK
CALIFORNIA

Regional Offices and Laboratories

Southern California Laboratories
820 Mission Street
South Pasadena, California

Washington Office
808 17th Street, N.W.
Washington 6, D.C.

New York Office
270 Park Avenue, Room 1770
New York 17, New York

Detroit Office
1025 East Maple Road
Birmingham, Michigan

European Office
Pelikanstrasse 37
Zurich 1, Switzerland

Japan Office
911 Iino Building
22, 2-chome, Uchisaiwai-cho, Chiyoda-ku
Tokyo, Japan

Representatives

Honolulu, Hawaii
1125 Ala Moana Blvd.
Honolulu, Hawaii

London, England
19, Upper Brook Street
London, W. 1, England

Milan, Italy
Via Macedonio Melloni, 49
Milano, Italy

Toronto, Ontario, Canada
Room 710, 67 Yonge St.
Toronto, Ontario, Canada