Solid Solubilities of Impurity Elements in Germanium and Silicon*

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The available data on solid solubilities of impurity elements in germanium and silicon are summarized in the form of solidus or solvus curves. New solubility data are presented for the lead-germanium, zinc-germanium, indium-germanium, antimony-silicon, gallium-silicon and aluminum-silicon systems. The correlation of the solid solubilities with the heats of sublimation and the atom sizes of the impurity elements is considered.

I. INTRODUCTION

In recent years a large amount of data has been obtained on the solid solubilities of impurity elements in germanium and silicon. Such data are of obvious practical importance in the semiconductor device field, where controlled impurity distributions are required. Of theoretical interest is the fact that, in favorable cases, these data can be used to provide information on heats and entropies of solution, binding energies and other thermodynamic properties of the solid solutions. In addition, one might hope that the attempts to interpret and correlate the relatively large amount of data on germanium and silicon will lead to a better understanding of the factors affecting solid solubility in other materials.

The purpose of this paper is to summarize and evaluate the experimental solid solubility data for germanium and silicon binary alloy systems. Included in this summary are some new data derived from crystal pulling and thermal gradient crystallization experiments. The use of a modified form of the distribution coefficient is illustrated by considering the empirical correlation of solid solubility with atom sizes and heats of sublimation of the impurity elements. A detailed consideration of the theoretical interpretation of the solid solubility data will be presented in a subsequent paper.[1]

II. SUMMARY OF SOLID SOLUBILITY DATA

For many systems the only available solid solubility data are values of $k°$, the distribution coefficient of the impurity element at the melting point of germanium or silicon. Table I summarizes what, in the author's opinion, are the best estimates of $k°$ presently available.* The remaining solid solubility data are summarized in Figs. 1 and 2 as plots of the solidus (solid-liquid equilibria) and, in some cases, the solvus (solid-solid equilibria) curves.† In plotting these curves the melting points of germanium[2] and silicon were taken as 937°C and 1410°C, respectively. The latter value is in agreement with Olette's value[3] of 1412 ± 2°C and Pell's value[4] of 1408 ± 2°C. In the following discussion the sources of the distribution coefficient and solid solubility data are discussed for each impurity element. While no attempt is made to give a complete bibliography of the work in this field, enough references are given to permit the interested reader to find further references to practically all of the work known to the author as of June 1959. Of particular value have been the papers of Burton,[5] Hall[6,7] and Tyler,[8] in which a considerable amount of data has been collected.

2.1 *Solid Solubilities in Germanium*

Lithium. The solidus curve in Fig. 1 is taken from Pell's solid solubility measurements[9] in the range from 593° to 899°C. Pell obtained a value of 1.6×10^{-3} for $k°$ by extrapolating these data to the melting point of germanium. A value of 0.002 is given in Table I because of the uncertainties involved in the 38° extrapolation and in the assumption made by Pell that the liquidus curve could be estimated by using a regular solution model. Pell's flame analyses appear more reliable than the electrical measurements of Reiss, Fuller and Morin[10] above the eutectic tem-

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* In this paper the distribution coefficient, k, is defined as $k = x_S/x_L$, where x_S and x_L are the atom fractions of the impurity element in the solidus and liquidus alloys, respectively. Frequently, values of k are reported in terms of concentrations; i.e., $k_c = c_S/c_L$, where c represents the concentration of the impurity element. For small concentrations of impurity in the solid and liquid phases $k = k_c(d_L/d_S)$, where d_L and d_S are the densities of liquid and solid germanium or silicon, respectively. However, in many cases it is unclear whether account was taken of the density change of germanium or silicon on melting or whether k or k_c is reported. No attempt is made here to correct k_c values since the correction is only about 5 per cent for germanium and 10 per cent for silicon. For most impurity elements this correction is less than the experimental uncertainty in k.

† In Figs. 1 and 2, the numbers following symbols refer to the references from which these points were taken. Where no number is given, the points are taken from the present work. Where a number and no symbol is given, the curve is based at least in part on the work in the reference quoted but no experimental points are given from that reference.

TABLE I — DISTRIBUTION COEFFICIENTS AT THE MELTING POINTS OF
GERMANIUM AND SILICON

Element	Germanium	Silicon
Lithium...................	0.002	0.01
Copper....................	1.5×10^{-5}	4×10^{-4}
Silver....................	4×10^{-7}	—
Gold.....................	1.3×10^{-5}	2.5×10^{-5}
Zinc......................	4×10^{-4}	$\sim 1 \times 10^{-5}$
Cadmium..................	$>1 \times 10^{-5}$	—
Boron....................	17	0.80
Aluminum.................	0.073	0.0020
Gallium..................	0.087	0.0080
Indium...................	0.001	4×10^{-4}
Thallium.................	4×10^{-5}	—
Silicon...................	5.5	1
Germanium...............	1	0.33
Tin......................	0.020	0.016
Lead.....................	1.7×10^{-4}	—
Nitrogen..................	—	$<10^{-7}(?)$
Phosphorus...............	0.080	0.35
Arsenic...................	0.02	0.3
Antimony.................	0.0030	0.023
Bismuth..................	4.5×10^{-5}	7×10^{-4}
Oxygen...................	—	0.5
Sulfur....................	—	10^{-5}
Tellurium.................	$\sim 10^{-6}$	—
Vanadium.................	$<3 \times 10^{-7}$	—
Manganese................	$\sim 10^{-6}$	$\sim 10^{-5}$
Iron......................	$\sim 3 \times 10^{-5}$	8×10^{-6}
Cobalt....................	$\sim 10^{-6}$	8×10^{-6}
Nickel....................	3×10^{-6}	—
Tantalum.................	—	10^{-7}
Platinum..................	$\sim 5 \times 10^{-6}$	—

perature. Reiss and Fuller[11] have calculated the solvus curve, plotted in Fig. 1, taking into account ion-pairing and hole-electron equilibria.

Copper. The solubility of copper in germanium has been studied quite extensively by a number of authors. The solidus curve in Fig. 1 is based in part on the Hall effect measurements of Woodbury and Tyler,[12] whose data above 650°C are in good agreement with the work of Finn[13] and Hodgkinson,[14] and especially with the equilibrium radiotracer measurements reported by Fuller et al.[15] However, more recent tracer and conductivity measurements of Wolfstirn and Fuller[16] yield somewhat higher solubilities, especially at the higher temperatures. The solidus curve in
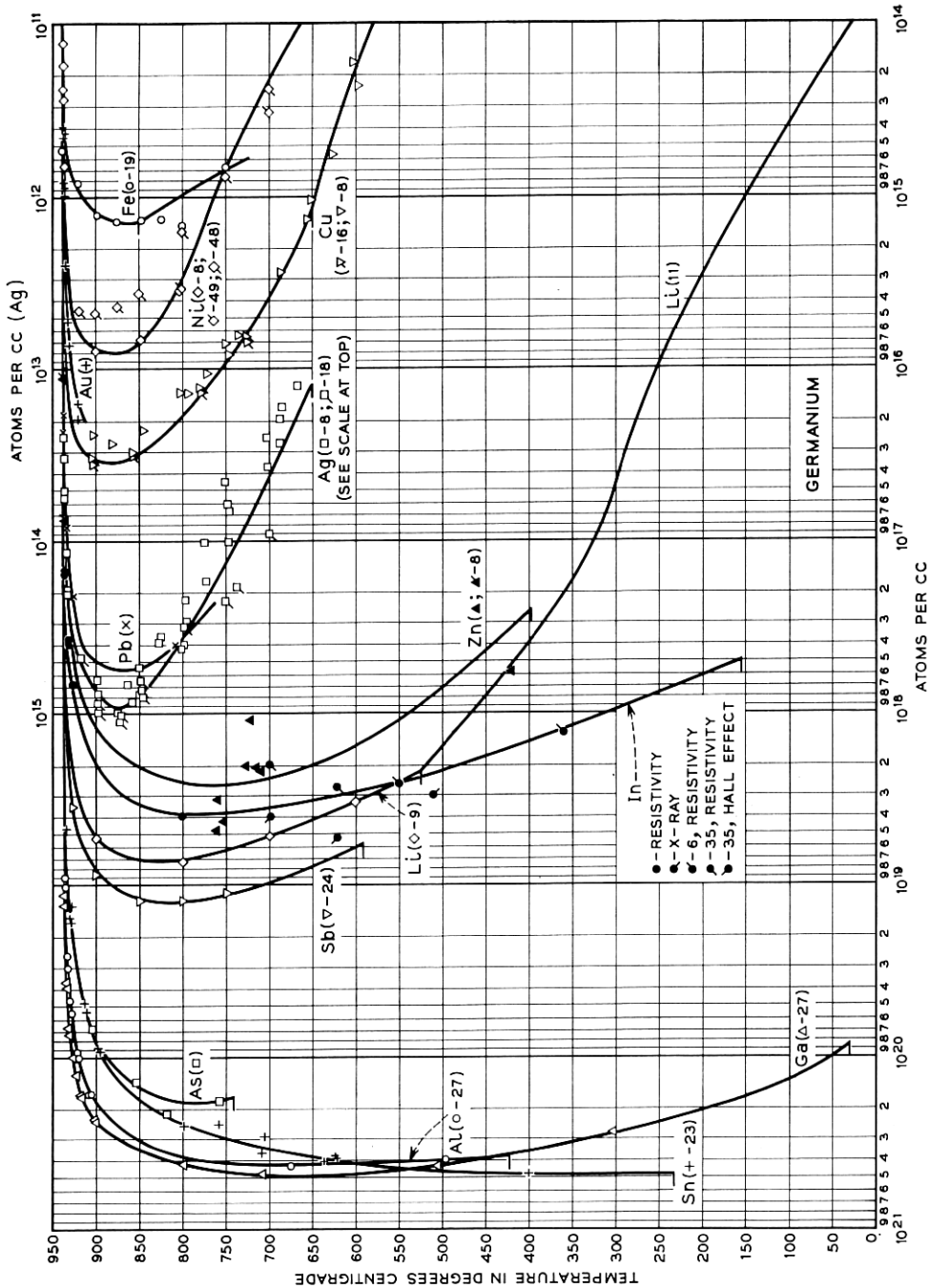
Fig. 1 favors Wolfstirn and Fuller's data at the higher temperatures and Woodbury and Tyler's data at lower temperatures. Below the eutectic temperature the latter authors' solubilities are significantly lower than the previous values determined from electrical measurements,[14,15] probably due in part to the failure of the earlier workers to consider deeper energy levels in interpreting their data. The value for $k°$ of 1.5×10^{-5} given in Table I was taken from the crystal pulling measurements of Burton et al.[17]

Silver. The value of 4×10^{-7} for $k°$ was obtained by Tyler[8] from Hall effect measurements on crystals pulled at temperatures ranging from 0.7 to 5 degrees below the melting point of germanium. This value of $k°$, which is orders of magnitude lower than the value of 10^{-4} reported by Burton et al.[17], is, however, consistent with the tracer data of Bugay, Kosenko and Miseliuk[18] and with Tyler's Hall effect data at lower temperatures. These data[8,18] were used to construct the solidus and solvus curves in Fig. 1. The temperature data of Bugay et al. appear to be somewhat questionable since, in their work on silver and on iron,[19] measurements were reported extremely close to or slightly above the melting point of germanium, 937°C, used in this paper.

Gold. The value of 1.3×10^{-5} for $k°$ was obtained by Tyler[8] from Hall effect measurements on crystals pulled at temperatures ranging from about 0.2 to 17 degrees below the melting point of germanium. This figure compares favorably with the value of 1.5×10^{-6} reported by Dunlap,[20] and is lower than the figure of 3×10^{-5} obtained by Burton et al.[17] Aside from Tyler's data near the melting point of germanium, no other solidus curve data are available.

Zinc. The value of 4×10^{-4} for $k°$ was obtained by Tyler and Woodbury[8,21] from Hall effect measurements on crystals pulled at temperatures ranging from about 0.1 to 2 degrees below the germanium melting point. This value is in disagreement with the figure of 0.01 due to Burton et al.,[17] but is consistent with low-temperature solubility data obtained by the author. The latter data were obtained from spectrophotometric analyses of the zinc content of crystals grown from zinc-germanium melts in a thermal gradient using methods described previously.[22,23] These results, although not very precise, are somewhat lower than reported by the author in an earlier paper,[24] and are summarized in Table II, where x_{Zn}^{s} is the atom fraction of zinc in the solidus alloy at the temperature, T. It is apparent that the solidus curve in Fig. 1 is uncertain by at least a factor of two, and that further work is needed.

Cadmium. The value of $>1 \times 10^{-5}$ was taken from Woodbury and Tyler.[8,25] No other solid solubility data are available.

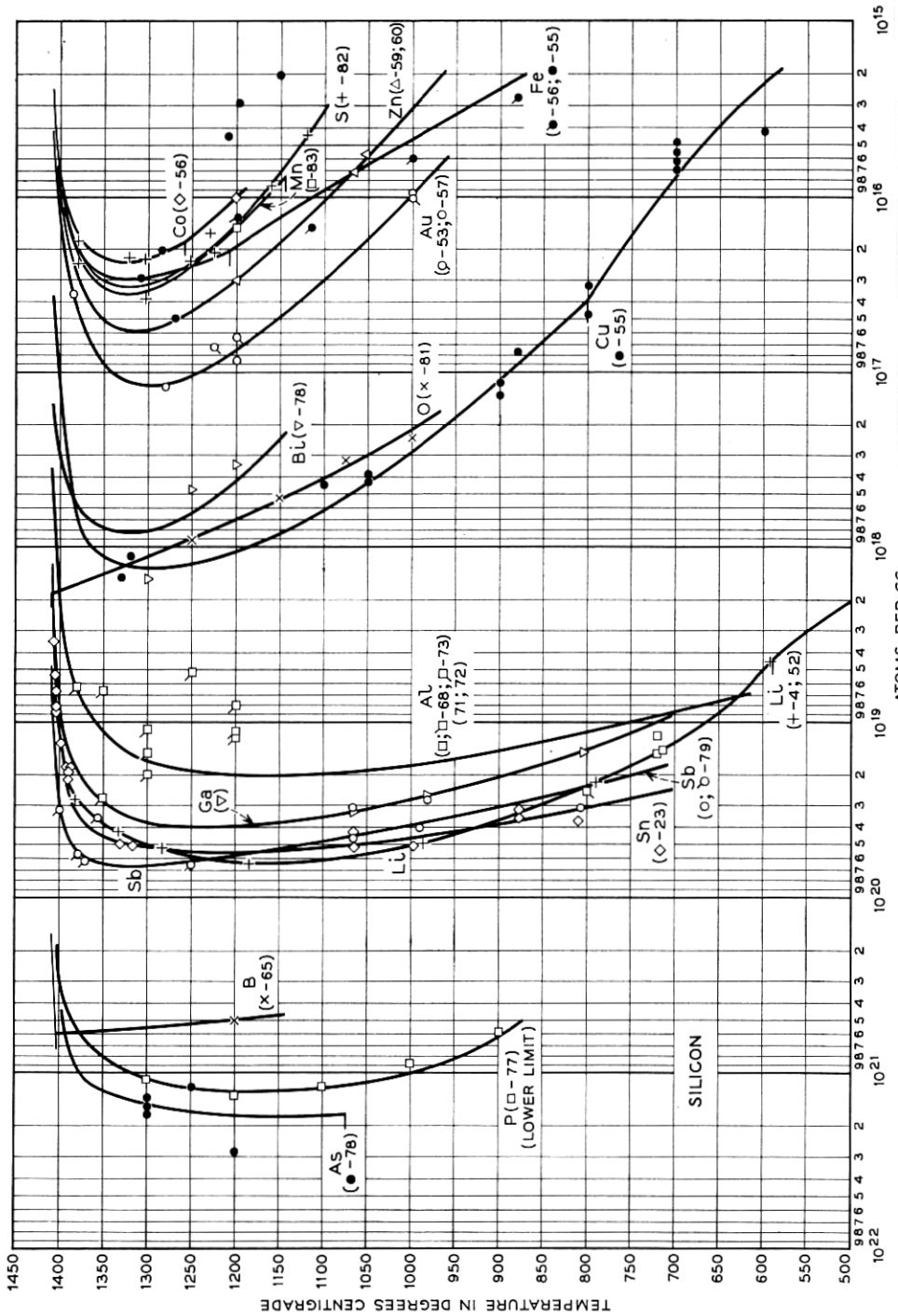*Boron.* The value of 17 for $k°$ was obtained by Bridgers and Kolb[26]

TABLE II — SOLID SOLUBILITY OF ZINC IN GERMANIUM FROM THERMAL
GRADIENT EXPERIMENTS

Temperature, in °C	x^8_{Zn}
420 ± 20	$(1.3 \pm 0.7) \times 10^{-5}$
709 ± 10	$(4.9 \pm 0.8) \times 10^{-5}$
714 ± 10	$(4.7 \pm 0.6) \times 10^{-5}$
720 ± 10	$(2.4 \pm 0.2) \times 10^{-5}$
725 ± 10	$(4.6 \pm 2.3) \times 10^{-5}$
752 ± 10	$(9.8 \pm 4.9) \times 10^{-5}$
759 ± 10	$(7.2 \pm 0.3) \times 10^{-5}$
760 ± 10	$(1.1 \pm 0.1) \times 10^{-4*}$

* This value was obtained by spectroscopic analysis while the other figures
are the results of spectrophotometric analyses. The uncertainties quoted in this
table represent the spread in the results of analyses on different portions of the
same sample.

from a study of the effect of growth rate on k. No other solid solubility
data are available.

Aluminum. The value of 0.073 for $k°$ and the solidus curve in Fig. 1
are taken from the work of Trumbore, Porbansky and Tartaglia[27] based
on chemical analyses of crystals grown by pulling and thermal gradient
techniques. Support for the validity of these results is found in the
internal consistency of chemical and electrical measurements on the
same crystals reported by Trumbore and Tartaglia.[28]

Gallium. The value of 0.087 for $k°$ and the solidus curve in Fig. 1 are
also due to Trumbore, Porbansky and Tartaglia.[27] A discussion of most
of the previous work on both aluminum and gallium is given in their
paper. The value of $k°$ is in agreement with the work of Bridgers and
Kolb,[29] who obtained a value between 0.085 and 0.01, and with the
recent value of 0.085 due to Leverton.[30] Leverton's value of 0.085 is prob-
ably a value of k_c and if corrected to k using his density for liquid
germanium would be $\sim$0.095. This figure is probably slightly high be-
cause of his relatively large pull rates.

Indium. Burton et al.,[17] Hall,[31] Dowd and Rouse[32] and Leverton[30]
have obtained values for $k°$ between 0.001 and 0.0013 from tracer and/or
conductivity measurements on pulled crystals. In the author's opinion,
the values 0.0012–0.0013 are probably high because of the relatively
large pull rates used in these experiments.[30,32] Evidence that $k°$ *may* be
as low as 7×10^{-4} has been obtained by the author from resistivity meas-
urements on sections of 16 crystals pulled under a variety of growth con-
ditions. The results of these experiments are summarized in Fig. 3(a),
which is a plot of the resistivity as a function of the amount of indium

in the melt. All of these crystals were pulled at a rate of 0.5 cm per hour. The "small" crystals were between 5 and 8 mm in diameter, while the "large" crystals were between 19 and 28 mm in diameter. Unfortunately, chemical analyses of these crystals proved to be unreliable, so that no independent check of the impurity concentration could be made. However, if the resistivity versus concentration curve of Ref. 28 is used, distribution coefficients can be calculated. (Over most of the concentration range, these calculations are essentially based on the assumption in Ref. 28 that the degenerate Hall effect formula, $R_H = 1/pe$, is valid.) The results of these calculations are summarized in Fig. 3(b), where the calculated distribution coefficient is plotted as a function of the melt composition.

A very interesting feature is immediately apparent from Fig. 3. The set of "small" crystals pulled in the [100] direction at $\sim$60 rpm gives
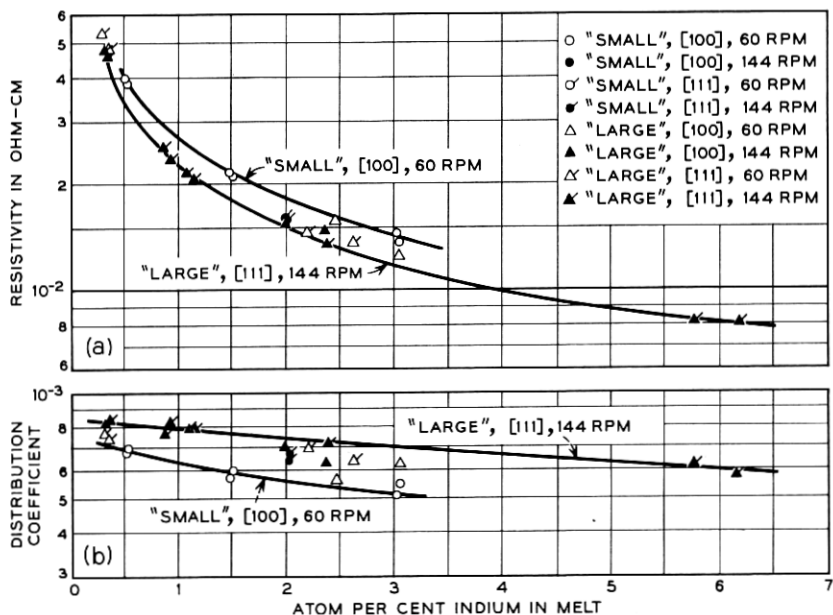

Fig. 3 — Distribution coefficient of indium in germanium as a function of melt composition in crystal pulling experiments. The values of k plotted in (b) were obtained from the resistivity measurements in (a) and the resistivity-concentration curves in Ref. 28. The points designated as corresponding to crystals rotated at 60 rpm correspond in some cases to rotation rates of 57 rpm and, for the point corresponding to 3.05 per cent indium in the melt, the rate was 50 rpm. With one exception all crystals were pulled at 0.5 cm/hr. One crystal (corresponding to the point at 2.03 per cent indium in the melt) was pulled at 0.1 cm/hr.

lower values of k than the set of "large" crystals pulled in the [111] direction at 144 rpm. Evidence that the size of the crystal is the most important factor determining the effective distribution coefficient is found in the fact that "large" crystals pulled in the [100] direction at either 144 or 57 rpm give effective k's significantly larger than the "small" [100] crystals. Also "small" [111] crystals rotated at 144 rpm give effective k's smaller than "large" crystals pulled under similar conditions. The cause of this size effect is not clear. Perhaps it is related to the thermal gradient effects discussed by Jillson and Sheckler[33] and by Goss.[34] Another possible explanation is that the larger true growth rate ($\sim$20 per cent larger) for the "large" crystals would lead to a larger effective k as discussed by Burton et al.[17] However, at the low growth rates of 0.5 and 0.6 cm per hour this would be expected to be a small effect. This statement is supported by the fact that two "small" crystal ([111], 144 rpm) gave the same effective k's, within experimental error, even though the pull rates were 0.5 and 1 cm per hour. Other obvious factors that could be playing a role are orientation, rotation rate, shape of interface, etc. The value of 0.001 for $k°$ given in Table I represents a compromise between the apparent upper and lower limits.*

The solidus curve at lower temperatures is also not clearly established. Hall[6] presented evidence that the solidus curve obtained by Thurmond and Kowalchik[24] was in error. The latter authors analyzed crystals of germanium recovered from slowly cooled indium-germanium melts. The author has obtained some relatively crude data from thermal gradient experiments which qualitatively confirm Hall's criticism of the earlier data. However, Hall's data do not appear to be just upper limits of the solid solubility as he suggested. Rather, in the author's opinion, they seem to be reasonably good estimates of the true solid solubility. Support for this opinion is given also by the work of John,[35] whose liquidus and resistivity data can be reinterpreted in the light of the liquidus data of Thurmond and Kowalchik[36] and using the resistivity data in Ref. 28. These data are summarized in Table III. The curve plotted in Fig. 1 is drawn to give a reasonable fit to Hall's data and to the data in Table III. Near the melting point of germanium only a few of the lower points from the crystal pulling experiments in Fig. 3 are plotted.†

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* Recently Thurmond[37] has proposed an interesting model for crystal growth. A consequence of this model is the possibility that an effective distribution coefficient *lower* than the equilibrium value might be obtained at finite growth rates.

† The X-ray measurements of Mack[38] on indium-germanium alloy p-n junctions indicate an indium concentration of about 6×10^{18} atoms per cc in the regrowth layer. The temperature corresponding to this concentration is of necessity rather uncertain, but it is apparently in the range of from 400 to 600°C.

TABLE III — LOW-TEMPERATURE SOLUBILITY DATA ON THE
INDIUM-GERMANIUM SYSTEM

Temperature, in °C	n_{In}^S (atom/cc)	Source	Remarks
~620	5.4×10^{18}	John[35]	from Hall measurement
~620	2.7×10^{18}	John[35]	from ρ measurement and Ref. 28
~700	3.8×10^{18}	John[35]	from Hall measurement
~700	2.0×10^{18}	John[35]	from ρ measurement and Ref. 28
~800	4.0×10^{18}	this work	from ρ measurement and Ref. 28
~510	3×10^{18}	this work	from X-ray measurement of lattice constant assuming Vegard's law and Pauling's tetrahedral radius for indium[37]
~300	$<1 \times 10^{19}$	this work	from ρ measurement and chemical analysis

Thallium. The value of 4×10^{-5} for k° is taken from Burton et al.[17] No other data are available.

Silicon. The value of 5.5 was obtained by Thurmond[38] from an analysis of the germanium-silicon phase diagram and from crystal pulling experiments. The solidus curve was determined by Stöhr and Klemm,[39] whose work has been confirmed in part by Hassion, Goss and Trumbore.[40] This system differs from all other known germanium and silicon systems in that a series of homogeneous solid solutions is formed. The reader is referred to Thurmond[41] for a plot of the phase diagram and a discussion of this system.

Tin. All of the tin data were taken from the work of Trumbore, Isenberg and Porbansky.[23] Their value of 0.020 for k° is in agreement with the work of Struthers quoted by Burton.[5]

Lead. The value of 1.7×10^{-4} for k° was obtained by the author from spectrophotometric analyses on four crystals pulled at 0.5 cm per hour. The results of these experiments are summarized in Table IV. One might speculate that the lower k value for the [100] crystal is due to an orientation effect, although more data are obviously needed. In addition, an analysis was made on one crystal grown by the thermal gradient tech-

TABLE IV — RESULTS OF CRYSTAL PULLING EXPERIMENTS ON THE
LEAD-GERMANIUM SYSTEM

Growth direction	Rotation rate, in rpm	x_{Pb}^L	k
[100]	144	0.00259	1.61×10^{-4}
[111]	144	0.00296	1.76×10^{-4}
[111]	144	0.0106	1.74×10^{-4}
[111]	144	0.0322	1.48×10^{-4}

nique, indicating that, at 805 $\pm$ 10°C, x_{Pb}^{S} = 8.9 $\times$ 10^{-6}. The solidus curve in Fig. 1 was constructed from these data assuming a simple solution model for the solid solutions as will be discussed in a subsequent paper.[1]

Phosphorus. The value of 0.080 for $k°$ was obtained by Hall,[7] who apparently pulled crystals from melts containing GaP and InP. This value compares with the earlier value of 0.12 due to Burton et al.[17]

Arsenic. The figure of 0.02 is due to Jillson and Sheckler[33] and compares with the value of 0.04 due to Burton et al.[17] and Hall.[31] The solidus curve in Fig. 1 is taken from Thurmond et al.[24] and is based on data obtained by the author from spectroscopic and spectrophotometric analyses of the germanium remaining after the evaporation of arsenic out of arsenic-germanium liquid alloys. These data are summarized in Table V. It should be noted that the evaporation technique requires considerable care and is very conducive to the production of occluded material. While there is no evidence to indicate that the data in Table V are not valid results, it would certainly be desirable to check these results by an independent method, e.g. by thermal gradient crystallization.

Antimony. The value of 3.0 $\times$ 10^{-3} for $k°$ in Table I is taken from Hall[7] and is in good agreement with the work of Burton et al.[17] and with the value of 3.3 $\times$ 10^{-3} (probably a value of k_c) obtained by Leverton,[30] whose value is probably slightly high because of the relatively large pull rate. This value of 3.0 $\times$ 10^{-3} is also consistent with the solidus curve derived from the tracer diffusion measurements of Thurmond and Kowalchik reported by Thurmond et al.[24]

Bismuth. The figure of 4.5 $\times$ 10^{-5} given for $k°$ in Table I is a compromise between the crystal pulling work of Burton et al.[17] and of Mortimer,[42] who obtained a value of 5 $\times$ 10^{-5} for crystals grown in a horizontal boat at 1$\frac{1}{2}$ inches per hour. However, Mortimer also gives a figure of 0.23 ohm-cm for a section of a crystal pulled at $\frac{3}{4}$ inch per hour, corresponding to a melt concentration of 1.3 per cent bismuth. Assuming the latter concentration to be weight per cent, the value of k using Prince's mobility data[43] would be 4 $\times$ 10^{-5}. At the germanium melting point, $k°$

TABLE V — RESULTS OF EVAPORATION EXPERIMENTS ON THE
ARSENIC-GERMANIUM SYSTEM

Temperature, in °C	x_{As}^{S}
905 $\pm$ 6	0.00155
853 $\pm$ 4	0.0032
818 $\pm$ 4	0.0049
757 $\pm$ 2	0.0041

would probably be somewhat higher than 4×10^{-5} but probably not 5×10^{-5}. No solidus data are available.

Sulfur, Selenium and Tellurium. Tyler[8] quotes maximum solid solubilities of sulfur, selenium and tellurium as $>5 \times 10^{15}$, $>5 \times 10^{15}$ and $>2 \times 10^{15}$ atoms/cc, respectively. A value for tellurium for $k°$ of $\sim 10^{-6}$ is given by Tyler.[8] No other data are available.

Vanadium. The value of $>3 \times 10^{-7}$ for $k°$ is from Woodbury and Tyler.[44] No other solidus data are available.

Manganese. The value of $\sim 10^{-6}$ for $k°$ is from Woodbury and Tyler[44] and Tyler.[8] No other solidus data are available.

Iron. The value of 3×10^{-5} for $k°$ was obtained by Bugay, Kosenko and Miseliuk,[19] who also determined the solidus curve. It should be noted that the temperature measurements of these authors appear to be somewhat doubtful, since their curve is extrapolated above the value of the melting point of germanium accepted in the present paper.

Cobalt. The value of $\sim 10^{-6}$ for $k°$ is from the resistivity measurements of Tyler, Newman and Woodbury,[45] whose results agree with the tracer work of Burton et al.[17] A maximum solid solubility of $\sim 2 \times 10^{15}$ atoms/cc is quoted by Tyler,[8] but no other details are given. A reasonable first approximation to the solid solubility at lower temperatures is probably given by the iron-germanium curve in Fig. 1.

Nickel. The value of 3×10^{-6} for $k°$ is from Tyler and Woodbury[46] and compares favorably with the earlier values of 5×10^{-6} due to Burton et al.[17] and 2.3×10^{-6} due to Tyler, Newman and Woodbury.[47] Solidus data have been obtained by Tyler and Woodbury,[8,46] while both solidus and solvus data were reported by van der Maesen and Brenkman.[48] In addition, Wertheim[49] has recently obtained solidus and solvus data from lifetime and conductivity measurements. Wertheim's solidus results are in good agreement with Tyler and Woodbury's solidus data, which are about a factor of two higher than the data of van der Maesen and Brenkman. The solidus curve in Fig. 1 favors Tyler and Woodbury's and Wertheim's data, while the solvus curve is from Wertheim, who is in agreement with van der Maesen and Brenkman where the data overlap.

Platinum. The value of $\sim 5 \times 10^{-6}$ for $k°$ is due to Dunlap.[50] No other solidus data are available.

2.2 *Solid Solubilities in Silicon*

Lithium. Pell[4] has determined the solidus curve from flame analyses of diffused crystals in the range from about 592° to 1382°C. Pell pointed out that the earlier solidus data of Reiss, Fuller and Pietruszkiewicz[51] were in error, as confirmed later by Fuller and Reiss.[52] Pell estimated a

value of 0.010 for $k°$ by extrapolating his solidus data to the melting point of silicon. Aside from the uncertainty in $k°$ due to the extrapolation, Pell had to assume regular solution behavior to estimate the liquidus curve. Hence, a value of 0.01 is given in Table I. The solvus curve in Fig. 2 is taken from Fuller and Reiss,[51,52] whose data appear reliable below the eutectic temperature.*

Copper. The value of 4×10^{-4} for $k°$ is taken from the work of Struthers,[53,54] who obtained a value of 4.5×10^{-4} from tracer analysis of crystals pulled at rates of about 10 or 20 cm per hour. Since a large pull rate was used, it is likely that Struthers' value is high. The solidus and solvus curves in Fig. 2 are based on the data of Struthers,[55] whose work has been confirmed by Collins and Carlson.[56] The shape of the solvus curve in Fig. 2 is slightly different from Struthers' curve, since an attempt has been made here to fit his data differently, in order to take into account the eutectic point.

Gold. The value of 2.5×10^{-5} for $k°$ is due to Collins, Carlson and Gallagher[57] and compares favorably with earlier values of 3×10^{-5} due to Taft and Horn[58] and to Struthers as quoted by Burton.[5] The solidus and solvus curves in Fig. 2 are based on the combined measurements of Collins et al.[57] and of Struthers.[53] The earlier work of Struthers[55] on gold is in error.[53]

Zinc. The value of $\sim 1 \times 10^{-5}$ for $k°$ is from Hall's treatment[6] of the data of Fuller and Morin,[59] but their results are divided by a factor of two, as suggested by Carlson.[60] A similar treatment of Fuller and Morin's data was used to estimate the solidus curve which was plotted to pass through the data from one radiotracer and two electrical measurements of Carlson.[60]

Boron. The value of 0.80 for $k°$ is quoted by Hall,[7] who refers to his earlier work[31] and that of Theuerer.[61] A value of 0.80 has also been obtained by Gould.[62] The work of Pearson and Bardeen,[63] when modified by the X-ray and density measurements of Horn,[64] may be interpreted as indicating a eutectic at roughly 3 to 7 degrees below the melting point, so that the solidus curve probably covers this limited temperature range. The solvus curve is also a very rough estimate based on a single point at 1200°C obtained by Howard[65] from diffusion measurements. Support for this curve has recently been obtained by Holonyak,[66] who found solubilities of $> 10^{20}$ atoms per cc in the range 700 to 800°C.†

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* The eutectic point for the lithium-silicon system shown in Fig. 2 is Pell's value of $590 \pm 10°C$. More recent work by Böhm[89] indicates a value of $635 \pm 10°C$.

† It now appears that the sheet resistivity curves used to interpret the boron diffusion data at 1200°C were in error. Although the correct curves are not yet available, the point given in Fig. 2 is probably low, perhaps by as much as a factor of 2 to 3.

Aluminum. The $k°$ value of 2.0×10^{-3} is taken from Hall,[7] who found this value to be consistent with the amount of aluminum required to compensate a given amount of antimony in the melt. Support for this figure, which compares with the value of $> 4 \times 10^{-3}$ quoted by Burton,[5] is found in some zone leveling experiments of Kolb and Tanenbaum.[67] The solidus curve has been the subject of a number of conflicting studies, the discrepancies being as high as three to four orders of magnitude in solid solubility at certain temperatures. R. C. Miller and Savage[68] have discussed critically the earlier works of Spengler[69] and Goldstein,[70] which represent the extreme values obtained for the solid solubility. More recently, Navon and Chernyshov[71] obtained a solidus curve from temperature gradient zone melting experiments which agree with Miller and Savage's scattered data at the higher temperatures. Similar agreement with the high-temperature data of Miller and Savage was obtained by Gudmundsen and Maserjian[72] by extrapolating their data obtained at lower temperatures in a study of the properties of regrowth layers. At low temperatures, however, there are appreciable discrepancies. From spectrophotometric and spectroscopic analyses on crystals grown in two thermal gradient experiments, the author obtained the results given in Table VI. S. L. Miller,[73] from capacitance measurements on p-n junctions, calculated a solubility of about 2.5×10^{19} atoms/cc at 800°C, a result that is more consistent with the data in Table VI. These figures are more than an order of magnitude larger than Navon and Chernyshov's solubilities and about a factor of 2 or 3 larger than the values of Gudmundsen and Maserjian at these temperatures. The discrepancy between these sets of data may be partially resolved by the use of Backenstoss' mobility data[74] extrapolated to higher impurity concentrations to interpret the resistivity data.[71,72] In constructing the solidus curve in Fig. 2, Gudmundsen and Maserjian's low-temperature curve, reinterpreted in this manner, was favored to represent a good compromise between the conflicting sets of data.

Gallium. The value of 8.0×10^{-3} for $k°$ is from the work of Hall,[7] who found this value to be consistent with the amount of gallium needed to

TABLE VI — RESULTS OF THERMAL GRADIENT EXPERIMENTS ON THE
ALUMINUM-SILICON SYSTEM

Temperature, in °C	x^S_{Al}
715 ± 10	0.00029 (spectrophotometric analysis)
720 ± 10	0.00024 (spectrophotometric analysis)
720 ± 10	0.00030 (spectroscopic analysis)

TABLE VII — RESULTS OF THERMAL GRADIENT EXPERIMENTS ON THE
GALLIUM-SILICON SYSTEM

Temperature, in °C	x_{Ga}^{S}
805 ± 10	3.0×10^{-4}
982 ± 10	5.2×10^{-4}
1066 ± 10	6.4×10^{-4}

compensate a given amount of antimony in the melt. The solidus curve in Fig. 2 was constructed using three results obtained by the author from spectrophotometric analyses of crystals grown at relatively low temperatures by a thermal gradient technique. These results are summarized in Table VII.

Indium. The value of 4×10^{-4} for k° is taken from Hall[7] and compares with the value of 5×10^{-4} quoted by Burton.[5] No solidus data are available, although Backenstoss[74] did obtain a solution of 4×10^{17} atoms/cc in pulled crystals, which would indicate a higher value for the maximum solubility.

Germanium. The value of 0.33 for k° was obtained by Thurmond[38] from crystal pulling experiments and an analysis of the germanium-silicon phase diagram.

Tin. The value of 0.016 for k° and the solidus curve in Fig. 2 are based on the work of Trumbore, Isenberg and Porbansky.[23] The value of k° compares with a figure of 0.02 due to Struthers quoted by Burton.[5]

Nitrogen. The value of $<10^{-7}$ for k° is from the work of Kaiser and Thurmond.[75] It should be emphasized that this figure represents only electrically active nitrogen and is not valid if nitrogen is electrically inactive in silicon. In the author's opinion, such a low value for k° seems rather unlikely in view of the correlations discussed later.

Phosphorus. The value of 0.35 for k° is taken from Burton[5] and Hall,[7] and is supported by the work of James and Richards.[76] No phase diagram is available,* but solid solubility data have been obtained from diffusion measurements reported by Mackintosh.[77] These solubilities, however, might not represent the true solid solubilities because of the possibility that, in the diffusion experiments involving P_2O_5, the phosphorus may have been dissolved in a glassy SiO_2 phase. Hence, the curve in Fig. 2 should probably be considered a lower limit.

Arsenic. The value of 0.3 for k° was taken from Burton.[5] The solidus

* Giessen and Vogel[90] have recently published a partial phase diagram for the silicon-phosphorus system. The silicon-rich liquidus curve was determined, and a Si-SiP eutectic temperature of 1131°C was measured.

curve in Fig. 2 was estimated from the scattered data obtained from capacitance measurements by Hassion and Russo.[78]

Antimony. The value of 0.023 for $k°$ is from Hall,[7] who found it to be consistent with the amount of antimony required to compensate given amounts of aluminum and gallium in the melt. The solidus curve was estimated from some diffusion measurements of Rohan, Pickering and Kennedy[79] and from data obtained by the author from spectrophotometric analyses of crystals grown in three thermal gradient experiments. The latter results are summarized in Table VIII. A resistivity of $\sim$0.0016 ohm-cm was found for one section of a crystal grown at 1066°C. Using the mobility data of Backenstoss,[74] the expected donor concentration would be $\sim$5 $\times$ 10^{19} atoms per cc, in reasonable agreement with the results in Table VIII.

Bismuth. The value for $k°$ of 7 $\times$ 10^{-4} is taken from a patent issued to Christian.[80] A rough estimate of the solidus curve is given, based on capacitance measurements of Hassion and Russo.[78]

Oxygen. The value of 0.5 for $k°$ was obtained by Thurmond[38] from a vacuum fusion gas analysis on a quenched silicon sample which was melted in a silica tube. The solvus curve is based on Hrostowski and Kaiser's work.[81]

Sulfur. The value of 10^{-5} for $k°$ and the solid solubility curve were taken from Carlson, Hall and Pell.[82] Since no germanium-sulfur phase diagram is available, it is not known whether this is a solidus and/or a solvus curve.

Manganese. The value of $\sim$10^{-5} for $k°$ is from Carlson.[83] One tracer measurement obtained by Carlson at 1200°C was used to obtain a rough estimate of the solidus curve.

Iron. The value of 8 $\times$ 10^{-6} for $k°$ is taken from the work of Collins and Carlson,[56] who obtained a value of 6 $\times$ 10^{-6} from tracer measurements and of between 5 and 10 $\times$ 10^{-6} from electrical measurements. These results are in accord with the tracer measurements of Struthers,[53]

TABLE VIII — RESULTS OF THERMAL GRADIENT EXPERIMENTS ON THE ANTIMONY-SILICON SYSTEM

Temperature, in °C	x_{Sb}^{S}
807 $\pm$ 10	6.2 $\times$ 10^{-4}
980 $\pm$ 10	5.6 $\times$ 10^{-4}
991 $\pm$ 10	8.1 $\times$ 10^{-4}
1066 $\pm$ 10	6.2 $\times$ 10^{-4}
1066 $\pm$ 10	9.3 $\times$ 10^{-4}

who has obtained a value of $\sim 10^{-5}$ for $k°$. The only solubility measure-ments above the eutectic temperature appear to be the tracer data of Struthers.[53,55] Struthers' data at the higher temperatures appear to be consistent with an extrapolation of the data of Collins and Carlson below the eutectic temperature. However, Struthers' data below the eutectic temperature disagree with Collins' and Carlson's data by as much as 2 or 3 orders of magnitude. It would appear that Struther's experiments, which include the "saturation" of silicon with iron as well as the calcu-lation of surface concentrations from short-time diffusion experiments, should rule out any complications due to slow and fast diffusing species, as suggested by Collins and Carlson. However, as pointed out by Collins and Carlson who checked Struthers' tracer measurements at 1200°C, the amount of iron used in the tracer experiments might have been insufficient in both sets of experiments to obtain the equilibrium solubility. Accordingly, the solvus curve in Fig. 2 has been arbitrarily drawn to favor Collins' and Carlson's data although, in the author's opinion, the discrepancy remains unresolved.

Cobalt. The value of 8×10^{-6} for $k°$ was obtained by Collins and Carl-son,[56] who also obtained a solid solubility of 1×10^{16} atoms/cc at 1200°C using tracer techniques. The curve plotted in Fig. 2 is an estimate based on these two figures.

Tantalum. The value of 10^{-7} for $k°$ is taken from Burton.[5] No other data are available.

Silver, Cadmium, Palladium. Collins and Carlson[56] state that the solid solubilities of these elements at 1200°C are from 10^{15} to 3×10^{16} atoms/cc as determined from tracer measurements. No other data are available.

2.3 *General Comments*

In the above discussion the author has made no attempt to assess the absolute accuracy of the experimental data. The temptation to do this was tempered by the fact that over the years there has been a pro-nounced tendency for the "accepted" equilibrium solid solubilities to decrease, even by orders of magnitude in certain cases. This tendency is quite understandable, in view of the recent development of more refined electrical and chemical techniques for determining impurity concentra-tions and of better techniques for the growth of single crystals free from occlusions and other imperfections. At the present time, it is likely that, even for the most carefully investigated systems, the accuracy of the data is no better than ± 10 to 20 per cent. Indeed, agreement to within a factor of two for different investigations is often considered good. While

for most semiconductor device applications such accuracy is sufficient, for thermodynamic studies it would be highly desirable to obtain accuracies of even better than ±10 per cent, if possible.

For further progress it seems that two general areas of experiment would be especially profitable. First, more work is needed on the direct correlation of chemical, tracer or other direct measurements of impurity concentration with resistivity and Hall effect measurements. Such work is particularly desirable in concentration ranges where the semiconductor is degenerate and where the relations between the Hall coefficient and the carrier concentration are in doubt. Second, more accurate work is needed on the effect of various crystal growth parameters on the solid solubility. The results for the indium-germanium system plotted in Fig. 3 appear to show an effect due to size, orientation, rotation rate or perhaps some other factor not immediately obvious. The very interesting work of Jillson and Sheckler[33] and of Goss[34] indicates possible effects due to thermal gradients, rotation, shape of interface, etc., on the effective distribution coefficient. Such studies, together with earlier works,[17,31] indicate that the accurate determination of equilibrium solid solubilities is subject to considerable complications. Along similar lines, it would be very worthwhile to carry out further experiments similar to those of John[35] and compare the crystal pulling and thermal gradient data at low temperatures.

III. CORRELATION OF SOLID SOLUBILITIES

The extent to which a solute element will dissolve in a solid solvent element is determined by the thermodynamic requirement that the compositions of the resulting solid solution and the coexisting solid, liquid or gaseous phase(s) must be such as to minimize the free energy of the system. Considerable work has been done on the correlation of the extent of primary solid solution with various properties of the solute and solvent elements, e.g. with atom size, valence, electronegativity, crystal structure, etc. (See, for example, Darken and Gurry.[84]) In such correlations a common practice is to compare maximum solid solubilities for various solutes as a function of the property in question. However, since the solid solubilities depend on the interactions between the solid solution and other phase(s), the maximum solid solubilities are not necessarily parameters that accurately indicate the relative compatibilities of the solute elements with the solvent element in solid solution.*

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* For example, if the bonds between a solute element, A, and a solvent, B, are stronger than A–A or B–B bonds, one might expect a solid solution of A in B to be relatively stable with a resulting high solubility of A in B. However, the relative

In the case of germanium and silicon systems, we are mainly concerned with the equilibrium between solidus and liquidus alloys. Here, the distribution coefficient is a desirable parameter for comparing the relative tendencies of various impurities to dissolve in solid germanium or silicon, since the effect of concentration in the liquid phase is taken into account. Thus, at the melting point of germanium or silicon the values of $k°$ can be thought of as giving the relative solid solubilities of the impurities, each at the same constant concentration (near infinite dilution) of impurity in the liquid phase and at essentially constant temperature.

Although the effect of liquid phase concentration is taken into account by using k as a solid solubility parameter, no account is taken of the effect of nonideal liquid solution behavior, i.e., of departures from Raoult's law. As discussed previously,[23] such departures can be taken into account by defining a new parameter

$$k' = \frac{x_S}{a_L} = \frac{k}{\gamma_L} = \frac{1}{\gamma_S} = \exp\left(\frac{\mu_L° - \mu_S}{RT}\right),$$

where a_L, γ_L and γ_S are the activity and activity coefficients, respectively, of the impurity in the liquidus and solidus alloys, based on a standard state of the pure liquid impurity element, and $\mu_L°$ and μ_S are the chemical potentials of the impurity in the pure liquid impurity and in the solidus alloy, respectively. The parameter k' is used here instead of $1/\gamma_S$ because of its similarity in form to the distribution coefficient. The parameter $k°'$ may also be considered as a solubility, in the sense that it represents the atom fraction of impurity in a hypothetical solid solution in equilibrium with the pure liquid impurity element.† As expected, k' is larger the more stable the solid solution, i.e., the smaller μ_S is compared to $\mu_L°$.

Let us now examine the use of k and k' in correlating solid solubilities with atom sizes. It was pointed out by Burton et al.[17] that a rough correlation exists between the tetrahedral radius of an impurity atom

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strength of the $A-B$ bond might also stabilize an intermetallic compound of A and B of a different crystal structure and decrease the amount of primary solid solution.[84] In such a case, the solid solubility itself does not accurately represent the stability of the solid solution relative to the pure components or, perhaps, relative to the solid solution of another solute element where no intermetallic compound is formed.

† This is a hypothetical solid solution in the sense that it must be assumed that γ_S remains constant even when the solid solution is no longer infinitely dilute, i.e., Henry's law must be obeyed. (The parameter $k°'$ may be considered a Henry's law constant.) Although this assumption may seldom be valid, $k°'$ is still a good measure of the stability of the infinitely dilute solid solution relative to the pure liquid impurity. It is in the dilute solution range where one can best obtain information about the basic solute-solvent interaction.

and its distribution coefficient in germanium at the melting point of germanium. In recent years a considerable body of additional data, including some substantial revisions of the earlier data, has been accumulated. Hence, it seems worthwhile to reconsider the situation for both germanium and silicon. In Figs. 4 and 5 the distribution coefficient at the germanium or silicon melting point is plotted as a function of the tetrahedral radius[37] of the impurity element.

For the case of germanium it is seen that elements from various groups of the periodic table tend to lie on different smooth curves. As expected there is a trend toward lower solubility as the radius of the impurity atom increases, with a relatively rapid decrease in $k°$ in the vicinity of 1.35 to 1.5Å. This decrease is in the neighborhood of a 15 per cent size difference between solute and solvent, where solid solubility becomes restricted in other alloy systems.[84] In the case of silicon, where the data
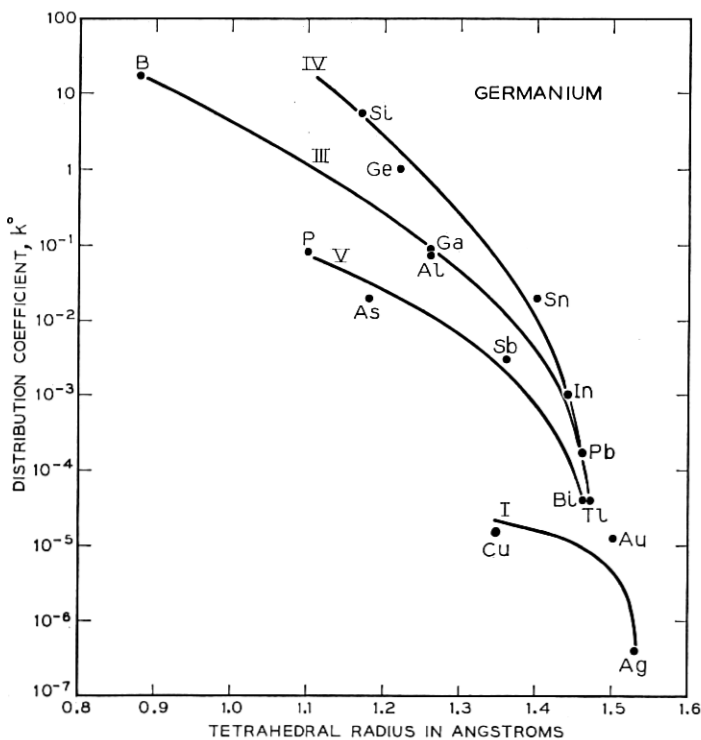
Fig. 4 — Distribution coefficients of impurities at the melting point of germanium as a function of the tetrahedral radii.
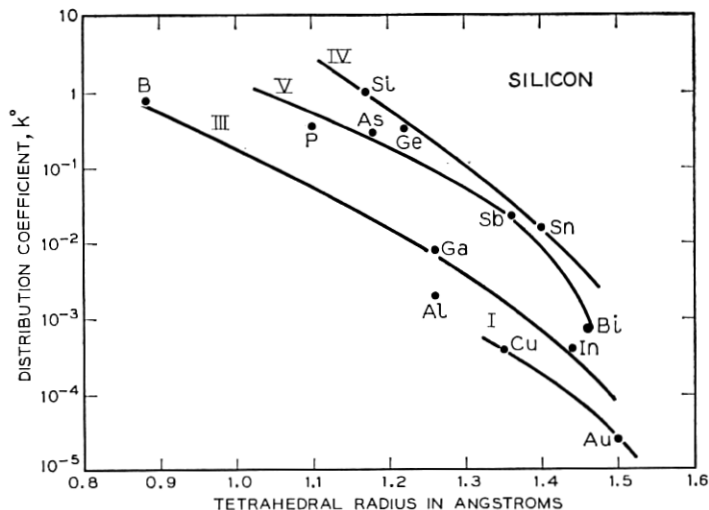
Fig. 5 — Distribution coefficients of impurities at the melting point of silicon as a function of the tetrahedral radii.

are fewer, similar trends are observed. A number of interesting differences should be noted, however. In germanium the relative order of $k°$ of elements from different groups is roughly IV > III > V, while for silicon the order is IV > V > III. Also, for the silicon case the discrepancy in size, i.e., the difference in tetrahedral radii of silicon and the impurity elements, for elements with a radius greater than 1.22Å, is greater than in the germanium systems. Yet there is little indication of the relatively sharp decrease in solubility found for germanium at 1.35 to 1.5Å. The elements gallium and aluminum are rather interesting in that they appear to have about the same tetrahedral radius and are in the same group of the periodic table. One might, therefore, expect them to have about the same distribution coefficients. While this is approximately true in the case of germanium, an appreciable difference is noted for the case of silicon.

Let us turn now to the consideration of correlations involving $k°'$. Unfortunately, there are no experimental data on values of $\gamma_L^°$ that must be evaluated to obtain $k°'$. However, the liquidus curve treatment discussed by Thurmond and Kowalchik[36] may be used to estimate the values of $\gamma_L^°$ to a first approximation. From these estimates of $\gamma_L^°$, estimates of $k°'$ have been made for those elements treated by Thurmond. These values are plotted against the tetrahedral radii in Figs. 6 and 7 for germanium and silicon.
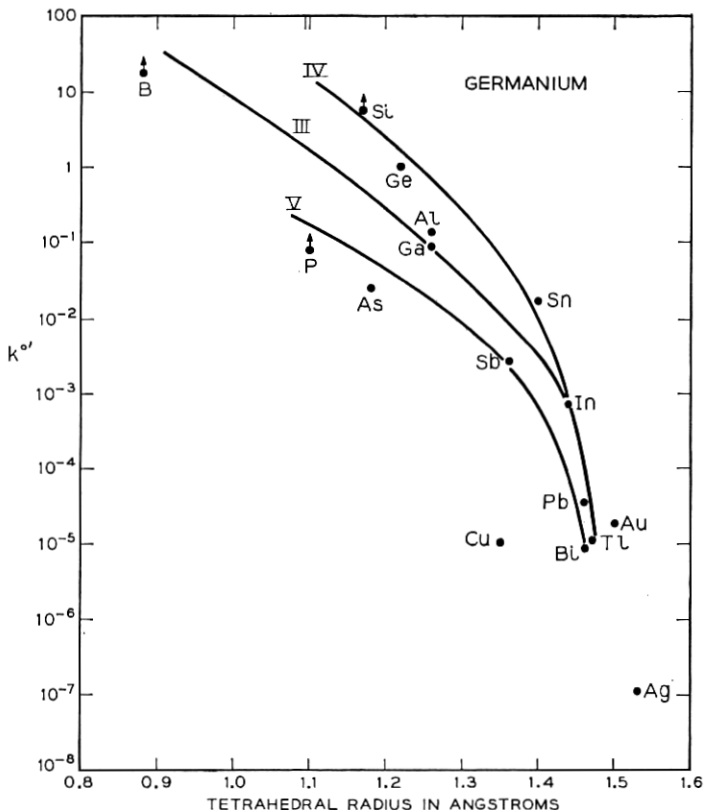
Fig. 6 — Plot of the parameter $k^{\circ\prime}$ versus the tetrahedral radii of the impurity elements for germanium. The arrows indicate the general direction of $k^{\circ\prime}$ where liquidus curve data are not available to estimate a value of $k^{\circ\prime}$.

For germanium there is not too much difference between the plots of k° and $k^{\circ\prime}$, due to the relatively small departures from ideality in the liquid phase. However, for silicon the shape of the curves is altered considerably by the use of $k^{\circ\prime}$. Although the data are relatively fewer, there is now evidence of a sharp decrease in solubility at the higher values of the tetrahedral radii, as in the case of germanium. It is also apparent that, in the case of silicon, the difference between gallium and aluminum has been altered significantly. A rather disturbing feature of some of the correlations is the anomalous behavior of gold, which does not fit smoothly into the pattern observed for the other elements. Aside from possible errors in k° or in the tetrahedral radius, it is possible that gold is substantially interstitial in the germanium or silicon lattice.

Another interesting feature of these correlations is that boron appears to fit relatively smoothly into the correlation, even though the difference in tetrahedral radii is very large, on the order of 25 to 30 per cent. Because of this difference, one might except a considerable reduction of solid solubility. If it is assumed that carbon and nitrogen behave similarly and fit on the curves for groups IV and V, respectively, the distribution coefficients of these elements should also be large, on the order of unity or perhaps significantly larger. However, in the case of nitrogen, Kaiser and Thurmond[75] suggest that $k°$ may be less than 10^{-7} in silicon, at least as far as electrically active species is concerned.

In treating the solid solubilities of tin in germanium and silicon, the distribution coefficient or k' was used to calculate the binding energies of tin in the semiconductor.[23] The binding energies were then related to the bond energies in pure tin, since the bond energy for gray tin is simply half the heat of sublimation to the monomeric vapor species. It was thought that a simple correlation might be expected to exist between solid solubilities and heats of sublimation of impurity elements of group IV and perhaps other groups of the periodic table. A theoretical treatment relating the distribution coefficient to bond energies and strain
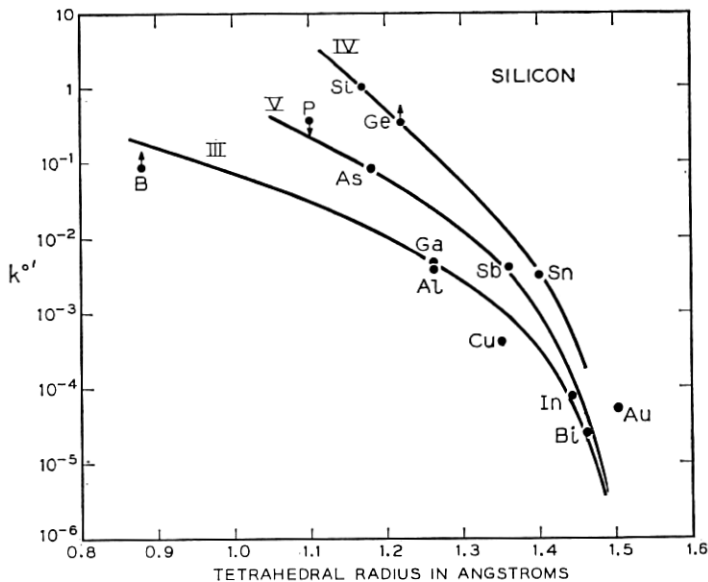

Fig. 7 — Plot of the parameter $k°'$ versus the tetrahedral radii of the impurity elements for silicon. The arrows indicate the general direction of $k°'$ where liquidus curve data are not available to estimate a value of $k°'$.

energies has recently been given by Weiser.[85] This treatment would also lead one to expect some sort of correlation between $k°$, $k°'$ and heats of sublimation or atom sizes. A rather striking correlation was found, especially for germanium, as is evident from Figs. 8 through 11, which are plots of $k°$ and $k°'$ as functions of the heats of sublimation of the solute elements. The heats of sublimation were taken principally from Honig.[86] No attempt was made to correct these heats to the melting points of germanium and silicon, since the form of the correlation would
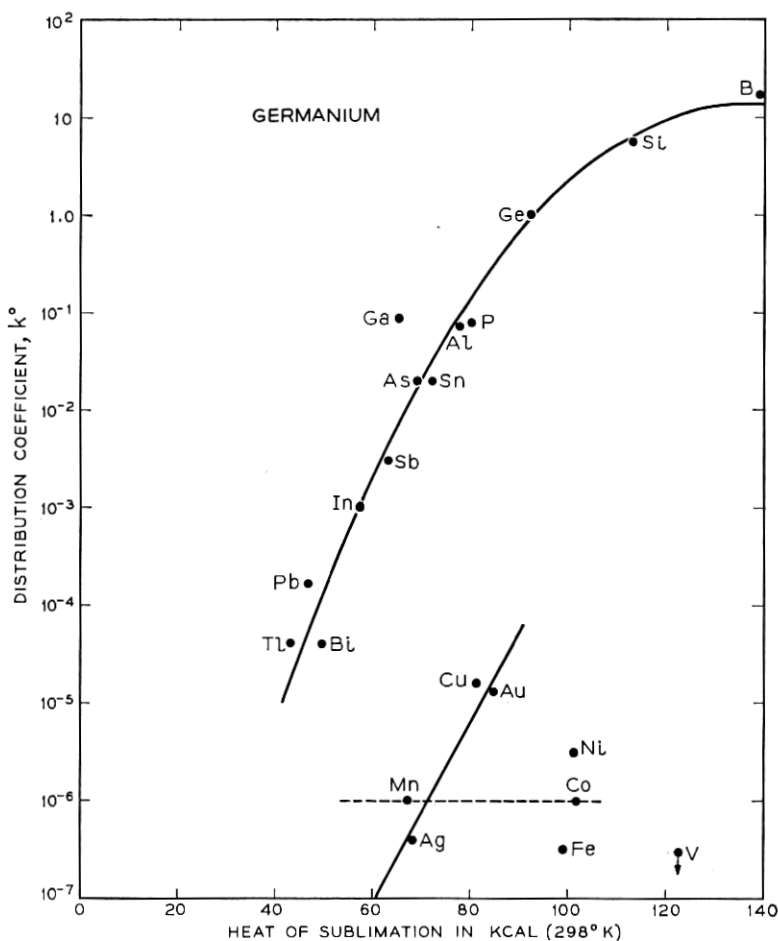
Fig. 8 — Distribution coefficients of impurity elements at the melting point of germanium as a function of the heats of sublimation of the impurities to the monomeric vapor species at 298°K.
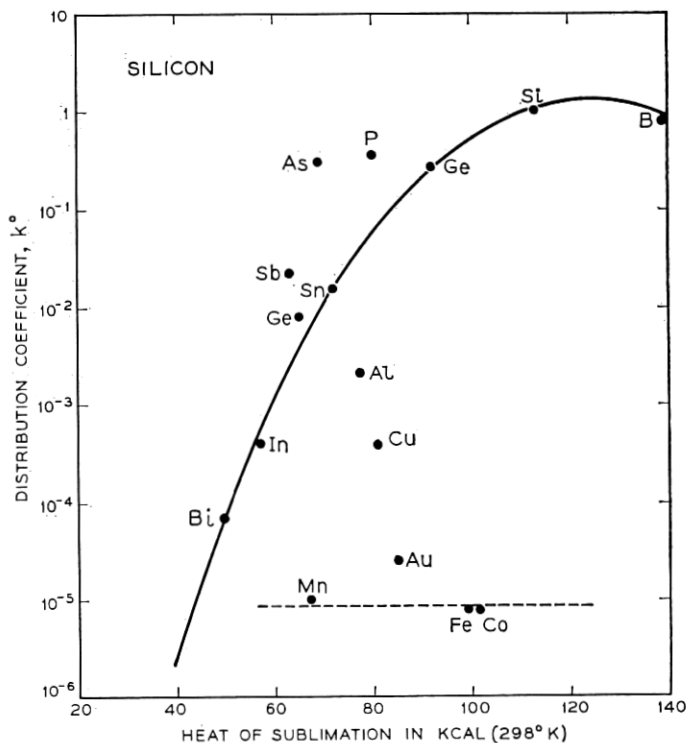
Fig. 9 — Distribution coefficients of impurity elements at the melting point of silicon as a function of the heats of sublimation of the impurities to the monomeric vapor species at 298°K.

not be affected significantly. It should be emphasized that these heats refer to the sublimation of the impurity element to the monomeric vapor species, not to the equilibrium vapor.

The most numerous and probably the most reliable data are on the germanium alloy systems. The outstanding feature of the correlation of both $k°$ and $k°'$ is the fact that, for germanium, elements of groups III, IV and V, with the exception of gallium, fall quite close to the same smooth curve. It is also seen that the copper-silver-gold and transition metal series fall into separate groups, with the latter group showing no evident trend of solubility with heat of sublimation.

In the case of silicon, where the data are fewer and probably less reliable, the plot of $k°$ bears only a qualitative resemblance to the behavior found for germanium. Turning to $k°'$, the situation improves somewhat, and one finds that the same general trends are present as in

germanium, although the fit of group III, IV and V elements to a single curve is questionable. The point for gold again seems anomalous, as was the case for the tetrahedral radius correlation.

The above correlations have involved the use of high-temperature data and theoretical assumptions about the nature of the liquid solu-
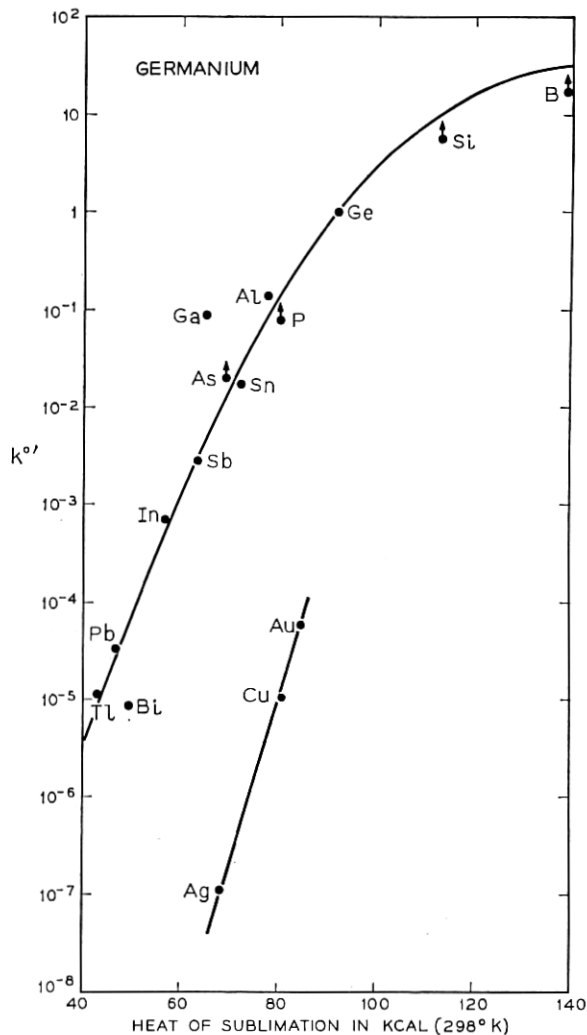

Fig. 10 — Plot of the parameter $k^{o\prime}$ for impurity elements in germanium versus the heats of sublimation of the impurities to the monomeric vapor species at 298°K. The arrows indicate the general direction of $k^{o\prime}$ where liquidus curve data are not available to estimate a value of $k^{o\prime}$.
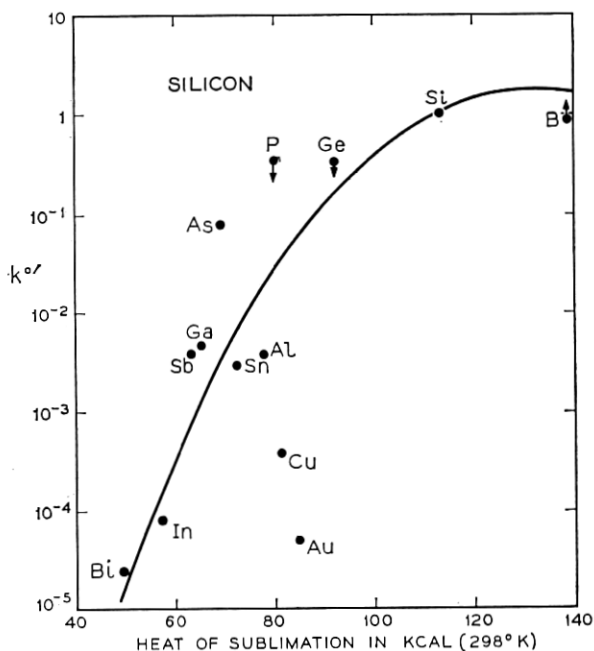
Fig. 11 — Plot of the parameter $k^{\circ\prime}$ for impurity elements in silicon versus the heats of sublimation of the impurities to the monomeric vapor species at 298°K. The arrows indicate the general direction of $k^{\circ\prime}$ where liquidus curve data are not available to estimate a value of $k^{\circ\prime}$.

tions. It is to be hoped that sufficient reliable data at lower temperatures can be obtained so that a comparison can be made in regions of the liquidus curves with smaller departures from ideality. Experimental work on activities of the liquidus alloys would be of great importance in interpreting the solid solubility data.

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REFERENCES

1. Trumbore, F. A. and Thurmond, C. D., to be published.
2. Hassion, F. X., Thurmond, C. D. and Trumbore, F. A., J. Phys. Chem., **59,** 1955, p. 1076.
3. Olette, M. Compt. rend., **244,** 1957, p. 1033.
4. Pell, E. M., J. Phys. Chem. Solids., **3,** 1957, p. 77.
5. Burton, J. A., Physica, **20,** 1954, p. 845.
6. Hall, R. N., J. Phys. Chem. Solids., **3,** 1957, p. 63.
7. Hall, R. N., in *Fortschritte der Hochfrequenztechnik,* Akademische Verlagsgesellschaft, M.B.H., Frankfurt am Main (to be published); also General Electric Research Lab. Report No. 58-RL-1874.
8. Tyler, W. W., J. Phys. Chem. Solids, **8,** 1959, p. 59.
9. Pell, E. M., J. Phys. Chem. Solids, **3,** 1957, p. 74.
10. Reiss, H., Fuller, C. S. and Morin, F. J., B.S.T.J., **35,** 1956, p. 535.
11. Reiss, H. and Fuller, C. S., J. Phys. Chem. Solids, **4,** 1958, p. 58.
12. Woodbury, H. H. and Tyler, W. W., Phys. Rev., **105,** 1957, p. 84.
13. Finn, G., Phys. Rev., **91,** 1953, p. 754.
14. Hodgkinson, R. J., Phil. Mag., **46,** 1955, p. 410.
15. Fuller, C. S., Struthers, J. D., Ditzenberger, J. A. and Wolfstirn, K. B., Phys. Rev., **93,** 1954, p. 1182.
16. Wolfstirn, K. B. and Fuller, C. S., J. Phys. Chem. Solids, **7,** 1958, p. 141.
17. Burton, J. A., Kolb, E. D., Slichter, W. P. and Struthers, J. D., J. Chem. Phys., **21,** 1953, p. 1991.
18. Bugay, A. A., Kosenko, V. E. and Miseliuk, E. G., Zh. tekh. fiz. (Moscow), **27,** 1957, p. 1671.
19. Bugay, A. A., Kosenko, V. E. and Miseliuk, E. G., Zh. tekh. fiz. (Moscow), **27,** 1957, p. 210.
20. Dunlap, W. C., Jr., Phys. Rev., **97,** 1955, p. 614.
21. Tyler, W. W. and Woodbury, H. H., Phys. Rev., **102,** 1956, p. 647.
22. Trumbore, F. A., J. Electrochem. Soc., **103,** 1956, p. 597.
23. Trumbore, F. A., Isenberg, C. R. and Porbansky, E. M., J. Phys. Chem. Solids, **9,** 1959, p. 60.
24. Thurmond, C. D., Trumbore, F. A. and Kowalchik, M., J. Chem. Phys., **25,** 1956, p. 799.
25. Woodbury, H. H. and Tyler, W. W., Bull. Amer. Phys. Soc., **1,** 1956, p. 127.
26. Bridgers, H. E. and Kolb, E. D., J. Chem. Phys., **25,** 1956, p. 648.
27. Trumbore, F. A., Porbansky, E. M. and Tartaglia, A. A., to be published.
28. Trumbore, F. A. and Tartaglia, A. A., J. Appl. Phys., **29,** 1958, p. 1511.
29. Bridgers, H. E., private communication.
30. Leverton, W. F., J. Appl. Phys., **29,** 1958, p. 1241.
31. Hall, R. N., J. Phys. Chem., **57,** 1953, p. 836.
32. Dowd, J. J. and Rouse, R. L., Proc. Phys. Soc. (London), **66B,** 1953, p. 60.
33. Jillson, D. C. and Sheckler, A. C., Phys. Rev., **98,** 1955, p. 229.
34. Goss, A. J., Marconi Rev., **22,** 1959, p. 18.
35. John, H., J. Electrochem. Soc., **105,** 1958, p. 741.
36. Thurmond, C. D. and Kowalchik, M., this issue, p. 169.
37. Pauling, L., *The Nature of the Chemical Bond,* Cornell Univ. Press, Ithaca, N. Y., 1945, p. 179.
38. Thurmond, C. D., private communication.
39. Stöhr, H. and Klemm, W., Z. anorg. allgem. Chem., **241,** 1935, p. 305.
40. Hassion, F. X., Goss, A. J. and Trumbore, F. A., J. Phys. Chem., **59,** 1955, p. 1118.
41. Thurmond, C. D., J. Phys. Chem., **57,** 1953, p. 827.
42. Mortimer, G., J. Electrochem. Soc., **105,** 1958, p. 731.
43. Prince, M. B., Phys. Rev., **92,** 1953, p. 681.
44. Woodbury, H. H. and Tyler, W. W., Phys. Rev., **100,** 1955, p. 659.

45. Tyler, W. W., Newman, R. and Woodbury, H. H., Phys. Rev., **96**, 1954, p. 874.
46. Tyler, W. W. and Woodbury, H. H., Bull. Amer. Phys. Soc., **2**, 1957, p. 135.
47. Tyler, W. W., Newman, R. and Woodbury, H. H., Phys. Rev., **98**, 1955, p. 461.
48. van der Maesen, F. and Brenkman, J. A., Phillips Res. Rep., **9**, 1954, p. 225.
49. Wertheim, G. K., Phys. Rev., **115**, 1959, p. 37.
50. Dunlap, W. C., Phys. Rev., **96**, 1954, p. 40.
51. Reiss, H., Fuller, C. S. and Pietruszkiewicz, A. J., J. Chem. Phys., **25**, 1956, p. 650.
52. Fuller, C. S. and Reiss, H., J. Chem. Phys. **27**, 1957, p. 318.
53. Struthers, J. D., private communication.
54. Thurmond, C. D. and Struthers, J. D., J. Phys. Chem., **57**, 1953, p. 831.
55. Struthers, J. D., J. Appl. Phys. **27**, 1956, p. 1560.
56. Collins, C. B. and Carlson, R. O., Phys. Rev., **108**, 1957, p. 1409.
57. Collins, C. B., Carlson, R. O. and Gallagher, C. J., Phys. Rev., **105**, 1957, p. 1168.
58. Taft, E. A. and Horn, F. H., Phys. Rev., **93**, 1954, p. 64.
59. Fuller, C. S. and Morin, F. J., Phys. Rev., **105**, 1957, p. 379.
60. Carlson, R. O., Phys. Rev., **108**, 1957, p. 1390.
61. Theuerer, H. C., Trans. A.I.M.E., **206**, 1956, p. 1316.
62. Gould, J. R., unpublished data.
63. Pearson, G. L. and Bardeen, J., Phys. Rev., **75**, 1949, p. 865.
64. Horn, F. H., Phys. Rev., **97**, 1955, p. 1521.
65. Howard, B. T., private communication.
66. Holonyak, N., Jr., unpublished data.
67. Kolb, E. D. and Tananbaum, M., J. Electrochem. Soc., **106**, 1959, p. 597; also Kolb, E. D., private communication.
68. Miller, R. C. and Savage, A., J. Appl. Phys., **27**, 1956, p. 1430.
69. Spengler, H., Metall., **9**, 1955, p. 181.
70. Goldstein, B., Bull. Amer. Phys. Soc., **1**, 1956, p. 145.
71. Navon, D. and Chernyshov, V., J. Appl. Phys., **28**, 1957, p. 823.
72. Gudmundsen, R. A. and Maserjian, J., Jr., J. Appl. Phys., **28**, 1957, p. 1308.
73. Miller, S. L., private communication.
74. Backenstoss, G., Phys. Rev., **108**, 1957, p. 416.
75. Kaiser, W. and Thurmond, C. D., J. Appl. Phys., **30**, 1959, p. 427.
76. James, J. A. and Richards, D. H., J. Elect. & Cont., **3**, 1957, p. 500.
77. Mackintosh, I. M., to be published.
78. Hassion, F. X. and Russo, L. J., private communication.
79. Rohan, J. J., Pickering, N. E. and Kennedy, J., J. Electrochem. Soc., **106**, 1959, p. 705.
80. Christian, S. M., U. S. Patent No. 2,820,185.
81. Hrostowski, H. J. and Kaiser, R. H., J. Phys. Chem. Solids, **9**, 1959, p. 214.
82. Carlson, R. O., Hall, R. N. and Pell, E. M., J. Phys. Chem. Solids, **8**, 1959, p. 81.
83. Carlson, R. O., Phys. Rev., **104**, 1956, p. 937.
84. Darken, L. S. and Gurry, R. W., *Physical Chemistry of Metals*, McGraw-Hill Book Co., New York, 1953, Ch. 4.
85. Weiser, K., J. Phys. Chem. Solids, **7**, 1958, p. 118.
86. Honig, R. E., R.C.A. Rev., **28**, 1957, p. 195.
87. Thurmond, C. D., in *Semiconductors*, Hannay, N. B., ed., Reinhold Publishing Corp., New York, 1959, Ch. 4.
88. Mack, G., Z. Physik, **152**, 1958, p. 26.
89. Böhm, H., Z. Metall., **50**, 1959, p. 44.
90. Giessen, B. and Vogel, R., Z. Metall., **50**, 1959, p. 274.