

reflection is no serious objection to the technical application of the effect. It can be shown that by the use of interferometric techniques in properly matched multilayer systems, a minute change in an optical system can be amplified to a considerably larger modulation.¹³

¹³ B. O. Seraphin, *J. Opt. Soc. Am.* **52**, 912 (1962).

ACKNOWLEDGMENTS

We are indebted to T. M. Donovan for help with the preparation of the samples, as well as to Dr. H. E. Bennett for advice on the optical part of the experiment. Dr. N. J. Harrick has made some valuable comments, which are included in the discussion part of this paper.

Solubility of Zinc in Gallium Arsenide

J. O. McCALDIN

North American Aviation Science Center, Canoga Park, California

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The distribution of tracer zinc-65 between the vapor and solid GaAs was studied. For dilute concentrations $[Zn_0]$ of zinc in the solid, the distribution coefficient K is a constant (Henry's law); at higher zinc concentrations, K falls off inversely with $[Zn_0]$. These observations can be interpreted simply in terms of an ionization equilibrium $Zn_0 \rightarrow Zn_0^- + e^+$. Based on this interpretation, the present measurements indicate an intrinsic carrier concentration n_i of about $4 \times 10^{18} \text{ cm}^{-3}$ for GaAs at 1000°C. This value is roughly six times larger than n_i estimated by extrapolation of Hall measurements; the latter, it is suggested, may reflect the presence of only the more mobile carriers.

The solubility of zinc was also studied as the arsenic pressure in the system was changed from the dissociation pressure (estimated 10^{-3} atm) to one atmosphere. The zinc solubility was observed to increase three- to fourfold with the increase in arsenic pressure. This result is in semiquantitative agreement with calculations for the mass action equilibrium of simple stoichiometric defects in GaAs.

I. INTRODUCTION

IMPUURITY solubility studies in semiconductors are favored by a relatively simple model for interpretation. The work of Reiss, Fuller, and Morin¹ on lithium in germanium and silicon showed how the Fermi level in the semiconductor host is a governing factor for the lithium solubility. In compound semiconductors like GaAs, where an additional thermodynamic degree of freedom is present, the solubility of an impurity depends not only on the Fermi level but also on the stoichiometric balance of the compound, e.g., the Ga-to-As ratio in GaAs. The stoichiometry of many of these compounds may be easily controlled, however, by fixing the vapor pressure of a volatile component, e.g., the arsenic pressure over GaAs.

In many compound semiconductors, furthermore, the effects of the Fermi level and of stoichiometry should be simply additive on a property like an impurity solubility. Consider, for example, the location of the Fermi level. This depends on the various ionization processes in the crystal and is dominated by those processes which involve relatively large concentrations. In GaAs at elevated temperatures, the intrinsic carrier concentration is of the order of 10^{18} cm^{-3} and fixes the location of the Fermi level, unless a chemical impurity is introduced at high concentration. Stoichiometric defects like vacancies and interstitials, being present at con-

siderably lower concentrations, e.g., 10^{15} cm^{-3} , would, therefore, not influence the Fermi level; they do, however, still influence properties like solubility by participating in the solubility reaction.² Thus a model for interpretation of solubility data in GaAs obtained by simply superposing the ionization equilibria¹ and the stoichiometric equilibria² seems reasonable. Such a model is discussed later in this paper.

The early work of Whelan *et al.*,³ on the behavior of Si in GaAs indicated several of the possibilities in solubility studies. In their interpretation they regarded the silicon as having a separate solubility on each sublattice of the host compound. Thus the net doping depended on the difference in silicon solubilities on the two sublattices. Quantitative agreement between this interpretation and experiment was obtained by them, particularly in regard to the influence of the Fermi level in controlling the two silicon solubilities.

Later experiments on Ge in GaAs by the present author⁴ and by Harada⁴ showed that stoichiometry could also be important, controlling the semiconductor type. These experiments have since been put on a

² D. G. Thomas, *Semiconductors*, edited by N. B. Hannay (Reinhold Publishing Corporation, New York, 1959), Chap. 7.

³ J. M. Whelan, J. D. Struthers, and J. A. Ditzenberger, *Proceedings of the International Conference on Semiconductor Physics, Prague 1960* (Czechoslovak Academy of Sciences, Prague, 1961), pp. 943-945.

⁴ J. O. McCaldin and Roy Harada, *J. Appl. Phys.* **31**, 2065 (1960).

¹ H. Reiss, C. S. Fuller, and F. J. Morin, *Bell System Tech. J.* **35**, 535 (1956).

quantitative basis by Vieland and Seidel⁵ in agreement with the interpretation of Whelan *et al.*³

A somewhat simpler system for solubility studies was introduced by Merten and Hatcher⁶ in their study of Zn in InSb. In this case only a single solubility is involved, as the zinc impurity normally occupies only the sites of one sublattice of the crystal. They observed a strong concentration dependence of the solubility, which they interpreted as due to certain kinetics of the experiment. An alternative possibility that is discussed later in this paper is that their measurements represent true (equilibrium) solubilities, which can be interpreted in terms of the Fermi level. They sought, but did not find an effect of stoichiometry.

Other studies by Fuller and Wolfstirn⁷ have dealt with Li in GaAs. Two species, a substitutional and an interstitial form of Li, seem to be important here. Fermi level effects, but not stoichiometric effects, were observed.

The possible importance of stoichiometry in these systems is suggested by diffusion experiments. Cunnell and Gooch⁸ have shown that zinc diffusion in GaAs is anomalous; they suggest that stoichiometry may be an important factor. The present author⁹ has shown that *p-n* junctions may be made to move through Ge-doped GaAs at different rates by varying the stoichiometry, and Vieland¹⁰ has shown that the diffusivities of many impurities in GaAs are strongly influenced by stoichiometry.

The present experiment was undertaken to measure concurrently both the Fermi level and the stoichiometric effects in a simple system. Provision was made to cover a wide range of these two variables in order to definitely establish their relative importance. A preliminary account of some early results of the present experiment has already been presented.¹¹

II. EXPERIMENTAL PROCEDURE

To compare the concentration of zinc in solution in gallium arsenide with its concentration in the surrounding vapor a simple experimental technique was used. The tracer zinc-65 was equilibrated between the solid gallium arsenide phase and a gas phase in a quartz capsule, as shown in Fig. 1(a). When the equilibration was completed, a cold finger was applied to one end of the quartz capsule, causing the gaseous zinc to condense there, as shown in Fig. 1(b). The capsule was then broken in two and the zinc-65 counted in each half of the capsule.

⁵ L. J. Vieland and T. Seidel, *J. Appl. Phys.* **33**, 2414 (1962).

⁶ Ulrich Merten and A. P. Hatcher, *J. Phys. Chem. Solids* **23**, 533 (1962).

⁷ C. S. Fuller and K. B. Wolfstirn, *J. Appl. Phys.* **33**, 2507 (1962).

⁸ F. A. Cunnell and C. H. Gooch, *J. Phys. Chem. Solids* **15**, 127 (1960).

⁹ J. O. McCaldin, *Bull. Am. Phys. Soc.* **6**, 172 (1961).

¹⁰ L. J. Vieland, *J. Phys. Chem. Solids* **21**, 318 (1961).

¹¹ J. O. McCaldin, *Bull. Am. Phys. Soc.* **7**, 235 (1962).

TABLE I. Purity of starting materials.

Material	Remarks
GaAs	Intrinsic, pulled crystal from Monsanto. Their Hall measurements give $\mu = 5800 \text{ cm}^2/\text{Vsec}$ and $n \approx 5 \times 10^{15} \text{ cm}^{-3}$.
Zinc	Supplied by Asarco as high purity. Spectrographic analysis detected only the following: [Mg], [Si], and [Cu] < 1 ppm, and [Pb] < 0.5 ppm. Chemical analysis indicated [Cd] = 0.14 ppm.
Arsenic	Supplied by Asarco as high purity. Spectrographic analysis detected only [Mg] < 0.5 ppm and [Cu] < 0.1 ppm.

A wafer of GaAs about 0.05 cm thick and weighing about 100 mg was used in each capsule. Extra arsenic could be added to the capsule. Thus the arsenic pressure under which the zinc equilibration occurred could be independently specified.

The completeness of the equilibration was checked in several of these experiments. In preliminary experiments the equilibration had been accomplished by solid-state diffusion of the zinc, but it was then observed that evaporation of the gallium arsenide across the diameter of the capsule afforded a more rapid equilibration. The evaporation method was used in all of the experimental runs reported in this paper. Various samples of the evaporated material taken from the same capsule showed variations in zinc concentration of about ten percent, which was considered adequate equilibration for the present purposes.

An important consideration in this experiment was the freedom of the system from unwanted impurities, particularly oxygen. The quartz capsules were baked overnight in flowing hydrogen at 1100°C prior to use. Care was taken in the handling of the other materials to minimize their exposure to oxidizing environments. In particular, the arsenic was received in evacuated capsules and stored in desiccators except for the few minutes required to load it into the capsules. Data on the chemical purity of the starting materials are shown in Table I.

The zinc-65 was prepared by neutron irradiation at Oak Ridge National Laboratory of the pure zinc de-

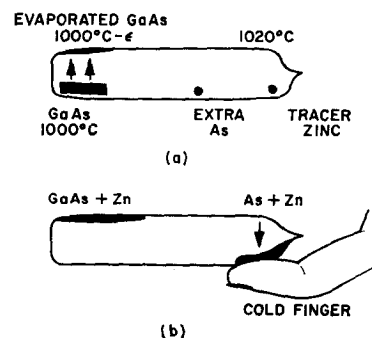


FIG. 1. Experimental arrangement. Equilibration at 1000°C occurred during evaporation of the GaAs across the diameter of the quartz capsule.

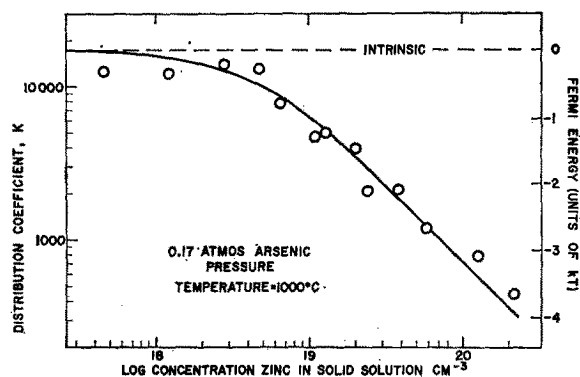


Fig. 2. The distribution of zinc between the solid GaAs phase and the vapor phase. The distribution coefficient is the ratio of zinc concentrations in the two phases. Corresponding values of the Fermi level based on the analysis in the text are also shown.

scribed in Table I. A weighed amount of zinc was sealed in an evacuated quartz capsule for each irradiation. The activity produced was then measured in a conventional scintillation well counter with spectrometer interposed between counter and scaler. In cases where the activity was so great as to overload the well counter, the zinc-65 source was removed various distances from the scintillation crystal and the count rate recorded. A comparison of the various zinc-65 sources was then made on a $1/R^2$ plot for consistency. Since zinc concentrations reported in this paper span almost five orders of magnitude, it was necessary to use several zinc-65 sources of different isotopic dilution.

Another consideration in the experiment was the possibility of the formation of a second condensed phase. Two such phases are known¹² in the Ga-As-Zn ternary system: $ZnAs_2$ and Zn_3As_2 . However, only the latter would be apt to form under the present conditions. An estimate of the pressures of zinc and arsenic needed to form condensed Zn_3As_2 at 1000°C can be had from the work of Silvey, Lyons, and Silvestri.¹³ They show a total vapor pressure of about 0.3 atm over stoichiometric Cd_3As_2 at its melting point (721°C), and it seems likely¹⁴ that the same pressure applies to Zn_3As_2 at its melting point (1015°C). From this information one can calculate that a concentration of zinc vapor of $1.3 \times 10^{18} \text{ cm}^{-3}$ would have been required at an arsenic pressure of 0.17 atm to form condensed Zn_3As_2 . The highest zinc vapor concentration used was $5 \times 10^{17} \text{ cm}^{-3}$. Furthermore, no change in the behavior of the distribution coefficient of zinc is apparent, in the results to be discussed, at the highest zinc concentrations, where Zn_3As_2 might form.

Also the work of Silvey *et al.*,¹³ indicates that the compounds in the zinc-arsenic system are dissociated in the vapor phase. Thus the only complication intro-

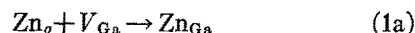
duced by polyatomic vapor species in the present experiment arises from the arsenic itself, as is discussed later.

III. RESULTS

A. Zinc Solubility at Arsenic Pressures Near One Atmosphere

The first experimental runs were performed under arsenic pressures in the range ordinarily used in GaAs preparation, i.e., a few tenths of an atmosphere. The most extensive data were obtained for 0.17-atm total arsenic pressure; these data are presented in Fig. 2. The ordinate in the figure is the distribution coefficient K which is the ratio of the zinc concentration $[Zn_s]$ in the solid phase to the concentration $[Zn_g]$ in the gas phase. Thus K is a measure of zinc solubility in GaAs.

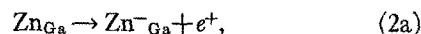
At low zinc concentrations K is constant (Henry's law), as might be expected for intrinsic GaAs. At higher values of $[Zn_s]$, however, K , and hence the zinc solubility, decrease. This situation is reminiscent of the well-known behavior¹ of lithium in silicon and germanium, so that the present results might be interpreted simply in terms of ionization equilibria. Following the analogy we write



for the combination of a zinc atom Zn_g in the gas phase with a vacant gallium site V_{Ga} in the crystal to yield a zinc atom on a gallium site Zn_{Ga} . The corresponding mass action is

$$P_{Zn} \times [V_{Ga}] = k_1 [Zn_{Ga}], \quad (1b)$$

where P_{Zn} is the external zinc pressure. The zinc atom in the crystal ordinarily ionizes



$$[Zn_{Ga}] = k_2 [Zn_{Ga}^-] p, \quad (2b)$$

where e^+ is a hole and p the hole concentration. Combining Eqs. (1b) and (2b), and approximating the total zinc concentration in the crystal as

$$[Zn_s] \approx [Zn_{Ga}^-] \quad (3)$$

since the ionization of the zinc is almost complete, we can represent the distribution coefficient

$$K = [Zn_s]/P_{Zn} = ([V_{Ga}]/k_1 k_2) 1/p = k_3 p^{-1}. \quad (4)$$

In the present example, we are treating the total arsenic pressure, and hence $[V_{Ga}]$, as constant.

Relation (4) appears to fit, at least qualitatively, the experimental data of Fig. 2. In intrinsic GaAs, where the hole concentration p is constant, the distribution coefficient K is constant. At high doping levels, however, K varies inversely with $p \approx [Zn_s]$, as expected.

The relation between hole concentration and zinc concentration can be represented over the full range of $[Zn_s]$ by

$$p = \frac{1}{2} \{ [Zn_s] + ([Zn_s]^2 + 4n_i^2)^{1/2} \}, \quad (5)$$

¹² Werner Koster and Werner Ulrich, *Z. Metallk.* **49**, 361 (1958).

¹³ G. A. Silvey, V. J. Lyons, and V. J. Silvestri, *J. Electrochem. Soc.* **108**, 653 (1961).

¹⁴ V. J. Lyons (private communication).

where n_i is the hole concentration in intrinsic GaAs, as shown in standard texts.¹⁵ Thus the distribution coefficient becomes

$$\log K = \log K_0 - \log \left\{ \frac{[Zn_s]}{2n_i} + [1 + ([Zn_s]^2/4n_i^2)]^{1/2} \right\}, \quad (6)$$

where K_0 is the distribution coefficient at "infinite dilution", i.e., in intrinsic GaAs. In fitting relation (6) to the present data, there are two adjustable parameters, K_0 and n_i . These parameters have been chosen to give a good fit in Fig. 2, yielding $K_0 = 17,800$ and $n_i = 4 \times 10^{18} \text{ cm}^{-3}$. The result for n_i is about 6 times larger than would be expected from Hall measurements, a point that is discussed in a later section of this paper. In general, however, the curve seems to fit within the random variations which are evident in the experimental points.

Arsenic pressures other than 0.17 atm were also studied in these early experimental runs. Some measurements made with 1.0-atm arsenic are shown in Fig. 3. The zinc solubility seems to be somewhat enhanced by the sixfold increase in arsenic pressure. However, the enhancement is comparable to fluctuations in the data points. Furthermore, the time required for equilibration is greater, the greater the arsenic pressure, and about one month was needed for equilibration at one atmosphere pressure. Thus the high arsenic pressure experiments were discontinued in favor of low arsenic pressures.

B. Zinc Solubility at the Dissociation Pressure

Early data in this experiment had clearly indicated the influence of the ionization equilibrium (i.e., the Fermi level) on the zinc solubility. However, the influence of stoichiometry which one might expect through the factor $[V_{Ga}]$ in relation (1b) evidently

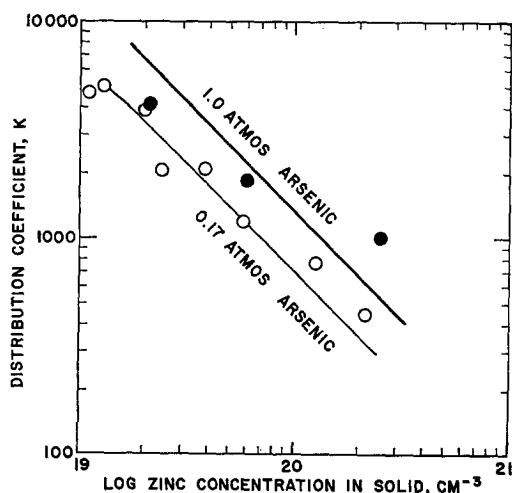


FIG. 3. Effect on the distribution coefficient of increasing the arsenic pressure from 0.17 to 1.0 atms. Data at 1.0 atm were obtained only in the extrinsic region.

¹⁵ W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).

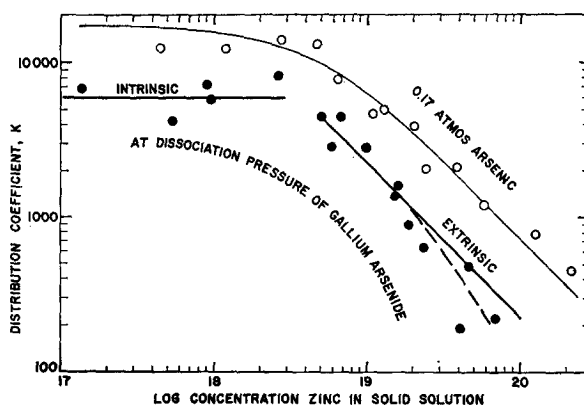


FIG. 4. Effect on the distribution coefficient of decreasing the arsenic pressure from 0.17 atm to the dissociation pressure.

would not be clearly demonstrated until a large change in arsenic pressure was introduced in the system. This was accomplished by performing experimental runs at the dissociation pressure, omitting the extra arsenic shown in the capsule of Fig. 1(a).

Unfortunately the dissociation pressure is not known accurately. The available data have been summarized recently, however, by Silvestri and Lyons.¹⁶ Their comparative plot of the somewhat conflicting data of various experiments suggests an average value of 10^{-3} atm for the dissociation pressure at 1000°C . This figure is used in the present paper as the best now available.

The distribution coefficient observed at the dissociation pressure is highlighted in Fig. 4, which permits comparison with K for 0.17 atm pressure. Evidently K is reduced about threefold by the change in pressure. The reduction cannot be determined accurately because of scatter in the data, and because K at the dissociation pressure seems to fall off more rapidly at high zinc concentrations than the above theory, relation (6), would anticipate. This last point is discussed later in the paper. Nevertheless, the qualitative fact that zinc solubility decreases as the arsenic pressure is decreased is exhibited clearly in Fig. 4.

The simple mass-action treatment described in part A indicates that the zinc solubility should behave in this way. The intrinsic distribution coefficient K_0 can be represented as $[V_{Ga}]$ divided by $k_1 k_2 n_i$ and, therefore, varies directly as the vacancy concentration. Thus the threefold shift in distribution coefficient in Fig. 4 suggests a similar change in vacancy concentration, $[V_{Ga}]$.

The vacancy concentration $[V_{Ga}]$ can be related to the arsenic pressure by consideration of the Schottky equilibrium in the crystal, a point that has been well discussed.¹⁷ The result is

$$[V_{Ga}] = k_7 P_{As}, \quad (7)$$

¹⁶ V. J. Silvestri and V. J. Lyons, *J. Electrochem. Soc.* **109**, 963 (1962).

¹⁷ J. J. Lander, in *Semiconductors*, edited by N. B. Hannay (Reinhold Publishing Corporation, New York, 1959), Chap. 2, p. 71.

TABLE II. Partial pressures (atm) of arsenic vapor species at 1000°C, as calculated from Stull and Sinke.^a

Total pressure	1 atm	0.17	10 ⁻³
Tetramers	0.937	0.142	1.4×10 ⁻⁴
Dimers	0.072	0.028	8.6×10 ⁻⁴
Monomers ^b	4.28×10 ⁻⁶	2.67×10 ⁻⁶	4.8×10 ⁻⁷

^a See reference 18.

^b The concentrations of monomers at the three pressures stand in the ratio 1.6:1:0.18.

where P_{As} represents the concentration of monatomic arsenic vapor. The actual arsenic vapor present under the experimental conditions described above is quite complex, consisting of tetramers and dimers as well as monomers. The relative concentrations of these species can be calculated from available thermodynamic data,¹⁸ however, and the results of such a calculation are presented in Table II. Since the present study involves equilibrium only, the only important specie is the one appearing in equilibrium (7), i.e., the monomer. The variations in its relative concentration should also occur in K , according to the present analysis. Table II indicates that the change from 0.17 to 1.0 atm pressure should cause a 60% increase in K , which is roughly what is observed in Fig. 3. The table also indicates that the change from 0.17 atm to the dissociation pressure should cause a 5.6-fold decrease in K , which may be compared to the observed threefold decrease. In view of the various uncertainties in these calculations, the agreement between analysis and experiment appears to be semiquantitative as far as the effect of arsenic pressure is concerned.

DISCUSSION

The solubility of zinc in GaAs is evidently subject to two influences. First, the zinc concentration itself is a strong influence, capable of causing the solubility to decrease some 30- or 40-fold, an effect we interpret here in terms of the Fermi level. Secondly, the stoichiometric balance in the host crystal is a somewhat weaker influence, capable of causing a solubility change of 3- or 4-fold in the conveniently accessible range of pressures in this system. Furthermore, the two influences seem to act independently of one another, judging from the parallelism of the solubility curves shown in Fig. 4. This fact supports the assumption of the model used here that the two influences are simply additive.

First we consider the influence of the zinc concentration itself. The observed concentration effect can be explained with some elementary semiconductor theory,¹ as has been shown; the essential point of the explanation is that high concentrations of dopant cause the Fermi level to move, thereby shifting all ionization equilibria in the crystal. A consequence of this interpretation is

¹⁸ D. R. Stull and G. C. Sinke, *Thermodynamic Properties of the Elements* (American Chemical Society, Washington, D. C., 1956).

that the intrinsic carrier concentration n_i at 1000°C is about $4 \times 10^{18} \text{ cm}^{-3}$, a value something like six times larger than is suggested by Hall measurements. No Hall measurements appear to have been made on GaAs at 1000°C, probably due to its volatility; however, one can extrapolate from the data of Whelan and Wheatley¹⁹ and Folberth and Weiss²⁰ to estimate $n_i \cong 7 \times 10^{17} \text{ cm}^{-3}$ at 1000°C, certainly within a factor of two. Thus the present experiment indicates a value of n_i definitely larger than the Hall concentration n_i .

A similar result was obtained in the experiments of Merten and Hatcher⁶ on the solubility of zinc in InSb near its melting point. In the case of InSb, Hall measurements of different observers^{21,22} agree that $n_i \cong 1.6 \times 10^{18} \text{ cm}^{-3}$ near the melting point. Yet the measured distribution coefficients of Merten and Hatcher, when analyzed in the same way as the present data, yield a value of $n_i \cong 3 \times 10^{19} \text{ cm}^{-3}$, i.e., about 20 times larger than the Hall concentration. Incidentally, our relation (6) can be fitted to their data about as well as to our own data; the principal difference is that their data fall more in the intrinsic region, ours mostly in the extrinsic region. Merten and Hatcher interpreted the discrepancy in the solubility and Hall values of n_i in terms of kinetic processes in their experiment, i.e., due to nonattainment of equilibrium in their "solubility" measurements.

In the present solubility measurements precautions were taken to insure a close approach to equilibrium, as described above. Still, a concentration n_i is measured which is several times the Hall n_i . We do not believe the discrepancy is due to nonattainment of equilibrium in the present measurements. Also we consider the Merten and Hatcher results still open to the interpretation that they too have a near-equilibrium measurement.

We offer an alternative explanation of the discrepancy by applying the argument about kinetics to the Hall measurement, rather than to the solubility measurements. The Hall measurement reflects a transport property, not an equilibrium property, and, therefore, can be strongly influenced by various relaxation times, competing reaction paths, and the like. Indeed Aukerman and Willardson²³ have already discussed a case in GaAs where the Hall measurement reflects carrier transport in two conduction bands, with the higher mobility band being strongly weighted in the statistical averaging that the Hall measurement does. Ehrenreich²⁴ in his review of the band structure of GaAs concludes that GaAs has, in addition to the [000] minimum, a second band in the [100] direction with minima $\sim 0.36 \text{ eV}$ above the [000] minimum. The second con-

¹⁹ J. M. Whelan and G. H. Wheatley, *J. Phys. Chem. Solids* **6**, 169 (1958).

²⁰ O. G. Folberth and H. Weiss, *Z. Naturforsch.* **10a**, 615 (1955).

²¹ O. Madelung and H. Weiss, *Z. Naturforsch.* **9a**, 527 (1954).

²² H. J. Hrostowski, F. J. Morin, T. H. Geballe, and G. H. Wheatley, *Phys. Rev.* **100**, 1672 (1955).

²³ L. W. Aukerman and R. K. Willardson, *J. Appl. Phys.* **31**, 939 (1960).

²⁴ H. Ehrenreich, *Phys. Rev.* **120**, 1951 (1960).

duction band has a high density-of-states so that at high temperatures it may be more populated than the [000] minimum. If one extrapolates the Aukerman and Willardson measurements to 1000°C, the second band is estimated to be populated with 2.5 times as many conduction electrons as the first band, which is the one emphasized by Hall measurements. This factor is not large enough to account for the above discrepancies in n_i . However, the numbers used in calculating the factor of 2.5 are not known sufficiently well to make a judgment yet. Also there are other features of both the GaAs and InSb band structures which are important for such a calculation and about which very little is known.

Let us turn now to the influence of stoichiometry on zinc solubility. Merten and Hatcher⁶ also looked for this effect. The negative result of their search for the effect seems now to be clearly due to the small variations in antimony concentration employed. They changed the antimony concentration by twofold, compared to a change of arsenic concentration in the present experiments by about a thousand-fold.

The magnitude of the stoichiometry effect is severely reduced in the present example by the presence of complexes in the vapor phase; as Table II indicates, a total change of a thousandfold in the arsenic vapor concentration results in only a ninefold change in the vapor specie of interest. More favorable systems to obtain a quantitative measure of the stoichiometry effect on solubility probably can be found in various oxides, where dimers are the only vapor complex. We have no plans for such studies, however.

One other point in the present experiments needs comment. In Fig. 4 the solubility curve for low arsenic pressure seems to fall off more rapidly at high zinc concentration than either the theoretical curve or the comparison experimental data. This tendency is illustrated in the figure by a dashed line. A similar tendency is present in Merten and Hatcher's data. If this tendency should indeed be real, it could be supporting evidence

for a defect proposed by Ruehrwein and Epstein,²⁵ namely, a zinc atom on an arsenic site Zn_{As} . This defect, unlike other defects currently being considered, would be favored by both low arsenic pressures and high zinc concentrations.

CONCLUSIONS

The present investigation of zinc in GaAs reveals a strong concentration dependence of the solubility, similar to earlier results⁶ on zinc in InSb. The present measurements at least are reasonably close to equilibrium, as judged by specimen homogeneity. The concentration dependence is interpreted as a Fermi level effect, with the consequence in the simple analysis given here that the intrinsic carrier concentration in GaAs at 1000°C is about $4 \times 10^{18} \text{ cm}^{-3}$. Extrapolated Hall measurements indicate a value roughly six times smaller, which may be due to the strong statistical weighting that a Hall measurement gives to high mobility carriers.

The present study also shows unmistakably that the stoichiometric balance in the host crystal affects the impurity solubility. A solubility increase of three- or fourfold was observed in this system as the total arsenic pressure was increased roughly a thousandfold. These results are in semiquantitative agreement with a simple analysis of the stoichiometric defects thought to be important in this system.

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Also the author wishes to thank U. Merten for a pre-publication copy of reference 6.

²⁵ R. A. Ruehrwein and A. S. Epstein, paper presented at the May 1962 meeting of the Electrochemical Society.