Journal of Physical and
Chemical Reference Data

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Cite as: Journal of Physical and Chemical Reference Data **6**, 1 (1977); https://doi.org/10.1063/1.555547

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Diffusion in Copper and Copper Alloys

Part V. Diffusion in Systems Involving Elements of Group VA

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A survey, comparison, and critical analysis is presented of data compiled from the scientific literature concerning diffusion in copper alloy systems involving elements in Group VA (As, Bi, N, P, Sb). Here the term "copper alloy system" is interpreted in the broadest sense. For example, the review of diffusion in the Cu-M system reports all diffusion situations which involve both copper and element M, including diffusion of Cu in M or in any binary, ternary, or multicomponent alloy containing M; diffusion of M in Cu or in any alloy containing Cu; and diffusion of any element in any alloy containing both Cu and M. Topics include volume diffusion, grain boundary diffusion, tracer diffusion, alloy interdiffusion, electromigration, thermomigration, strain-enhanced diffusion and diffusion in molten metals. An extensive bibliography is presented along with figures, tabular presentation of data, and discussion of results.

Key Words: Alloys; antimony; arsenic; bismuth; copper; diffusion; electromigration; liquid metals; nitrogen; phosphorus; ternary diffusion; thermomigration.

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1. Introduction

1.1. Organization of Review According to Alloy System

The present critical review is the fifth in a series designed to provide data on diffusion in copper and copper alloys. The first review [1] in the series covered copper self-diffusion. The second review [2] of the series dealt with diffusion in the copper-silver and copper-gold systems. The third review [3] analyzed diffusion in copper alloy systems which involved the elements of the Groups IA, IIA, IIIB, IVB, VB, VIB, and VIIB. The fourth review [4] covered diffusion in alloys of copper with the elements of Group VIII. The present review continues the coverage of diffusion in copper alloy systems. Data on diffusion in systems which involve copper and elements of Group VA are presented in this review. Succeeding reviews in this series will cover the remaining copper alloys.

Each Cu-M alloy systems (M=As, Bi, N, P, Sb) will be reviewed independently as a unit; and the references for each system are independently numbered. The term "copper alloy system" is interpreted in the broadest sense here. For example, the review of diffusion in the Cu-Sb system includes all diffusion situations which involve both copper and antimony. This same format will be followed for all Cu-M systems. According to this format, the Cu-Sb review treats:

1. Diffusion of antimony in pure copper
2. Diffusion of copper in pure antimony
3. Diffusion of copper or antimony in Cu-Sb binary alloys
4. Diffusion of impurities in Cu-Sb binary alloys
5. Diffusion in any ternary alloy containing both copper and antimony (or in any multicomponent alloy containing both copper and antimony)
6. Diffusion of copper in any alloy containing antimony
7. Diffusion of antimony in any alloy containing copper

For easy reference, a list of subsections is provided in the table of contents for each alloy system. Under the Cu-Sb system as an example, binary situations which involve only copper and antimony (items 1, 2, and 3 in the above list) are discussed first and are presented in separate subsections. Then, ternary situations involving a third element are presented. These ternary subsections appear in alphabetical order according to the chemical symbol of the third element. Data of types 4, 5, 6, and 7 all are included in each such subsection, if available. If no diffusion data are available on a given three-component system, for example Cu-Sb-M, then this system is simply not listed. Special diffusion effects, such as grain boundary diffusion, thermomigration, electromigration, etc., are discussed in a final set of subsections.

Diffusion measurements in quaternary and other higher-order multicomponent alloys are not common in copper alloy systems. General discussions of diffusion in these alloys are presented in a single subsection entitled, for example, Cu-As-X.

1.2. Methods Used To Present and Compare Data

The primary quantities of interest for diffusion are the diffusion coefficient, D, and the activation energy for diffusion, Q. The diffusion coefficient is defined by the equation

$$J=-D(\partial c/\partial x), \qquad (1)$$

where $\partial c/\partial x$ is the concentration gradient of the diffusing species along a direction x of interest, and the diffusion flux, J, is the amount of diffusing species crossing unit area normal to the x-axis per unit time. D, itself, is a constant of proportionality and usually is expressed in units of cm^2/s. Experimentally, D is usually found to depend exponentially on temperature according to an Arrhenius-type equation,

$$D=D_0 \exp(-Q/RT). \qquad (2)$$

Thus, a straight line is usually obtained when $\log D$ is plotted as a function of T^{-1}. Here, T is the absolute temperature, D_0 and Q are experimentally measured constants which can be determined from the intercept and the slope of that line, and R is the universal gas constant ($1.987\ \text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}=8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$).

The quantity Q in eq (2) is usually found expressed in the literature in units of kcal/mol, or in units of kcal alone (with the mole understood). Usually Q can be determined to only two or three significant figures and has a value between 10,000 and 100,000 cal/mol. Thus, when Q is expressed directly in terms of cal/mol, as is sometimes found in the literature, the last few zeros before the decimal are not significant figures. A second type of unit for Q frequently found in the literature is the electron volt or electron volt per atom. When this unit is reported, it is understood that R in eq (2) is replaced by Boltzmann's constant, k (equal to $1.3806\times10^{-23}\ \text{J}\cdot\text{K}^{-1}$ or $8.617\times10^{-5}\ \text{eV}\cdot\text{K}^{-1}$).

In alloys, the dependence of D and Q on alloy composition provides another variable which must be considered in addition to those previously discussed for self-diffusion in pure copper [1]. Usually no consistent general equation can be written to express $D(c)$ at all concentrations, c. Thus, data on the composition dependence of D or Q is usually summarized in this review by displaying the measured values on graphs of D or Q versus composition, rather than by use of equations.

When the temperature dependence of D is considered, the best smooth line through the data often can be summarized by expressing D in the form of eq (2). In the present paper, the more reliable data usually are presented in display equations in the text in this form. In addition, individual D_0 and Q values may be quoted to provide information in summary form and expedite comparisons between differing measurements. Even for the temperature dependence of D, however, the most useful means of presenting and comparing data probably is by means of graphs showing the diffusion coefficients themselves; in this case with log D plotted versus T^{-1}. A number of these graphs are shown in the present review.

The textual discussions provide commentary on the experiments reported and, wherever possible, a comparison and evaluation of the reliability of the experimental methods and results. Nevertheless, an attempt has been made here to provide comprehensive coverage and to provide some indication of diffusion behavior even in systems where only a few data are available.

In choosing among various reported diffusion measurements for reliability, the internal consistency and reproducibility of the data are considered important. For example, it is expected that the experimental points, expressed as log D, should fall very nearly on a straight line when plotted as a function of T^{-1}, as given by eq (2). The degree of scatter from a line drawn through the experimental points is usually assumed to provide a good indication of the accuracy of the data. Such a line may not be well-established if only a few measurements in a limited temperature range are reported. For this reason, data taken at many different temperatures and over a wide temperature range are usually considered more reliable (in the absence of other considerations).

At temperatures near the melting point, volume diffusion through regions of good crystal structure is normally predominant. At lower temperatures, diffusion along the easy paths provided by grain boundaries often becomes important. Most data reported in the literature are for diffusion at moderately high temperatures, above two-thirds of the melting point, where volume diffusion usually dominates. Nevertheless, grain-boundary diffusion measurements also are reported in the review when available. A separate diffusion coefficient, D_{gb}, for diffusion in a grain boundary can be defined from eq (1). A uniform D_{gb} value usually is assumed to apply to the entire grain-boundary volume, which is regarded as extending in two dimensions but having a finite width, δ. With the grain boundary regarded as a plane, one can say that the plane envisoned in eq (1) normal to the concentration gradient will cut the grain-boundary plane along a line. Experimentally, the flux, J', crossing unit length of this line often is the quantity measured rather than the actual flux, J, per unit area, which is the quantity in eq (1). In such a case, taking the ratio $J'/-(\partial c/\partial x)$ yields $D_{gb}\cdot\delta$. Thus, where grain-boundary diffusion results are quoted, $D_{gb}\cdot\delta$ frequently is given instead of just D_{gb}, with δ being an unknown grain-boundary width, and $D_{gb}\cdot\delta$ then being expressed in units of cm^3/s.

A similar situation can arise in surface diffusion measurements if the surface is regarded as having a thickness, δ. More commonly though, the surface concentration is expressed in terms of the number of atoms, c', per unit area (rather than the number per unit volume). Then, the ratio, $J'/-(\partial c'/\partial x)$, yields a conventional surface diffusion coefficient, D_s, which can be expressed in the conventional units of cm^2/s.

For descriptions of standard experimental techniques of measuring volume, grain-boundary, and surface diffusion coefficients, and related diffusion quantities, the reader is referred to general review articles [5–9]. In addition, specific references and comments are provided at points in the textual commentary where results from some of the less-standard types of measurements are discussed.

1.3. Different Types of Diffusion Coefficients

For diffusion in alloys, one must be particularly careful to establish the type of diffusion coefficient that is reported. There are two main types of diffusion experiments in alloys frequently reported in the literature—tracer diffusion and interdiffusion.

An understanding of why tracer and interdiffusion experiments, which both define their diffusion coefficients, D, by means of eq (1), yield different diffusion coefficient values can be gained by considering the physical arrangement of these measurements and the basic diffusion equations. The basic kinetic diffusion equation for the atom flux, J, of a diffusing species with respect to the end of a specimen can be written as

$$J=-D^*\frac{\partial c}{\partial x}+\langle v\rangle_F c+v_k c. \qquad (3)$$

Here, D^* is a quantity related to the atom jump frequencies of the diffusing species; $\langle v\rangle_F$ is the atom drift velocity from atomic driving forces; c is the concentration; and v_k is the velocity of the local lattice plane with respect to the end of the specimen. It may be noted that eq (3) is similar to eq (1) but differs in two respects: first, eq (3) contains two velocity-concentration terms, $\langle v\rangle_F c$ and $v_k c$, and secondly, the coefficient of $\partial c/\partial x$ in eq (3) is the specific quantity, D^* rather than a general diffusion coefficient, D.

In a typical tracer diffusion experiment, a very thin layer of tracer atoms is deposited on the surface of a homogeneous alloy, and diffusion is carried out in the absence of driving forces. Here, the tracer atoms diffuse into an essentially unchanging homogeneous matrix, and $\langle v\rangle_F$ and v_k are zero. Consequently, D^* is the measured diffusion coefficient in this type of experiment, which results in D^* being called the "tracer diffusion coefficient."

By contrast, in an interdiffusion experiment, two bulk specimens of different alloy composition are brought into contact, and atoms diffuse in both directions across the interface. These alloys usually have positive or negative energies of mixing, and atom drift velocities $\langle v\rangle_F$ can arise from forces created by gradients in these energies. Also, the D^* values of the various constituents usually are unequal. This inequality produces a net atom flux across the interface toward one end of the specimen and makes v_k differ from zero. In simple interdiffusion experiments, where other driving forces are absent, $\langle v\rangle_F$ and v_k are proportional to $\partial c/\partial x$, and J still is found to be directly proportional to $\partial c/\partial x$. However, if one calculates an interdiffusion coefficient, $\tilde{D}$, from the ratio $-J/(\partial c/\partial x)$, as in eq (1), one should expect to find $\tilde{D}\neq D^*$.

For a binary alloy, $\tilde{D}$ is the same for both constituents. Thus, there are two different tracer diffusion coefficients for the two constituents in a binary alloy (one for each constituent), but only one interdiffusion coefficient. The interdiffusion coefficient in some references is called the "chemical diffusion coefficient," or the "chemical interdiffusion coefficient."

The interdiffusion coefficient, $\tilde{D}$, in a binary alloy containing constituents A and B can be related to the tracer diffusion coefficients, D_A^* and D_B^*, for A and B atoms in that alloy by the equation

$$\tilde{D}=(N_A D_B^*+N_B D_A^*)\Phi S, \tag{4}$$

where N_A and N_B are the mole fractions of species A and B in the alloy, Φ is the thermodynamic factor, and S is the vacancy wind factor. When either N_A or N_B goes to zero, both Φ and S go to unity; so in the limit of a very dilute binary alloy, $\tilde{D}$ should equal the tracer diffusion coefficient of the dilute constituent. In nondilute alloys, ΦS can differ appreciably from unity, say by a factor of four. In these alloys, additional information (which is usually not available) on thermodynamic activity coefficients is neeeed to determine $\tilde{D}$ from D_A^* and D_R^*.

A third type of diffusion coefficient in alloys is the intrinsic diffusion coefficient, D_i^I. This coefficient is defined by eq (1) when J in that equation is defined as the atom flux of species i with respect to a local lattice plane. Equations relating D_i^I to other diffusion coefficients are given, for example, in reference 10. When v_k differs from zero, D_i^I will differ from $\tilde{D}$. When $\langle v\rangle_F$ differs from zero, D_i^I will differ from D_i^*.

In the discussion of D_i^I and $\tilde{D}$ given above, it was assumed that the only atomic driving force was that from the heat of mixing. If other driving forces of unknown magnitude are present in an experiment or if other lattice distortions contribute to v_k, the measured diffusion coefficient, $[-J/(\partial c/\partial x)]$, will, of course, be affected. Usually in these cases, one refers to an "effective diffusion coefficient" obtained from eq (1).

In situations where the measured J or $\partial c/\partial x$ values are believed to contain significant unknown errors, an "apparent diffusion coefficient" may still be defined based on the apparent values of J and $\partial c/\partial x$ (or of the other related quantities) which the particular experiment provides.

Diffusion coefficients may show a strong dependence on alloy composition. This composition dependence can lead to very non-symmetric concentration-versus-distance profiles in some interdiffusion experiments. If a non-symmetric profile is assumed to be symmetric, a single "average diffusion coefficient" can be calculated for the experiment. Other methods of finding an average diffusion coefficient applicable to a given concentration range may give somewhat different results, since the types of averaging may differ.

In ternary and higher-order multicomponent alloys, there will be more than one independent concentration gradient. Then, instead of defining a single diffusion coefficient as in eq (1), it often is convenient to define a set of partial diffusion coefficients, D_{ij}, where

$$J_i=-\Sigma_j D_{ij}\frac{\partial c_j}{\partial x}. \tag{5}$$

Here, J_i is the flux of species i, and $\partial c_j/\partial x$ is the concentration gradient of species j. Since the sum of the concentration gradients of all species in the crystal must equal zero, one of the concentration gradients must be eliminated from the general expression if one wishes to obtain independent, partial diffusion coefficients. This gradient can arbitrarily be chosen to be any one of the gradients, $\partial c_n/\partial x$. Then,

$$J_i=-\sum_{j\neq n} D_{ij}^n\frac{\partial c_j}{\partial x},$$

where

$$D_{ij}^n=D_{ij}-D_{in}. \tag{7}$$

For an n-component alloy, there are $n-1$ independent partial diffusion coefficients, D_{ij}^n, for each species i.

In multicomponent alloys, partial diffusion coefficients can be either intrinsic diffusion coefficients or interdiffusion coefficients. Here again, the distinction is that the intrinsic diffusion coefficients are related to the fluxes with respect to local lattice planes, whereas the interdiffusion coefficients are related to fluxes measured relative to the undiffused ends of the specimen.

Further discussion of the physical meaning of D^*, D^I, and $\tilde{D}$ can be found in references [2], [3], and [11].

1.4. Other Diffusion Related Quantities

In this review, the emphasis is on direct measurements of diffusion coefficients. There are, however, a number of diffusion-related phenomena, such as sintering, creep, gas-permeation rates, measurements of interface motion, and a variety of relaxation-time measurements, from which estimates of diffusion rates can be made. These data are reported when it appears that significant diffusion information can be obtained from them. For example, diffusion activation energies often can be estimated from these diffusion-related phenomena.

Temperature and alloy composition are the major variables usually considered in reporting diffusion data. Nevertheless, diffusion rates also can be influenced by a number of other factors, such as pressure, electric fields, temperature gradients, ultrasonic vibration, and strain rates. When appropriate data are available, separate descriptions are provided in the reviews which report on these special effects.

For diffusion as a function of pressure, p, it usually is possible to write

$$D=D(p=0)\exp(-p\Delta V/kT), \tag{8}$$

where $D(p=0)$ is the value of the diffusion coefficient at zero pressure, and ΔV is called the measured activation volume. For hydrostatic pressures on metals, very high pressures usually are required before D changes appreciably, since ΔV is usually of the order of an atomic volume.

In the case of diffusion in an electric field, a critical quantity in determining the diffusion rates is the measured effective charge, q^{**}, of the diffusing species, since the field E affects the drift velocity in eq (3) according to the equation

$$\langle v\rangle_F/D^*=q^{**}E(kT)^{-1}. \tag{9}$$

Here q^{**} may differ appreciably, however, from the actual charge of the diffusing species. For diffusion in a temperature gradient, the measured heat of transport, Q^{**}, serves a similar function, with

$$\langle v\rangle_F/D^*=-Q^{**}\nabla T/kT^2. \tag{10}$$

These quantities are discussed more fully, for example, in reference 1 and in other later reviews in this series.

Discussions also are given in reference 3 of the relation between gas permeation rates and diffusion. For example, if K is the permeation rate through an alloy, S is the solubility, and D the diffusion coefficient, one can write for diffusion-controlled permeation [12, 13]

$$K=DS. \tag{11}$$

In an interdiffusion experiment, the net shift with respect to the ends of the specimen in the position of the original interface lattice plane is called the Kirkendall shift, x_k. This shift, which results from unequal intrinsic diffusion of components across the plane, can be measured, for example, by placing inert wires or other markers at this plane. For normal parabolic diffusion at constant temperature for diffusion time τ, the Kirkendall shift will be proportional to $\tau^{1/2}$, since

$$x_k=\int_0^\tau v_k dt,$$

and v_k is proportional to $\tau^{-1/2}$. Here, v_k is the same velocity which appears in eq (3). For simple interdiffusion in a binary A–B alloy, v_k is proportional to $D_A{}^I-D_B{}^I$ and

$$x_k=2\tau(D_A{}^I-D_B{}^I)(\partial N_A/\partial x)_\tau. \tag{12}$$

In parabolic diffusion, $\partial N_A/\partial x$ is proportional to $\tau^{-1/2}$, so eq (12) yields $x_k\propto\tau^{1/2}$, as expected.

In binary alloys, $\tilde{D}$ is related to the intrinsic diffusion coefficients by

$$\tilde{D}=N_A D_B{}^I+N_B D_A{}^I. \tag{13}$$

If $\tilde{D}$ and x_k are measured at a binary alloy interface of known composition and concentration gradient, $D_A{}^I$ and $D_B{}^I$ can be found from eqs (12) and (13).

1.5. Note on References

When the original language of a reference is not in English, the language is specified in parentheses following the translated title. After this notation of language is the reference to the original publication and a reference to an English translation, if known to us, enclosed in brackets.

When the original reference is from a journal that is translated in "cover-to-cover" form, the name of the translated journal and its citation appears within brackets. A good source for obtaining the names and availability of these translated journals is reference 14.

If the original reference is not available in a "cover-to-cover" translated form, but an English translation is available, a note as to its availability is made with an abbreviated name (NTIS, NTC, BISI, etc.) and an order number. These are available from the following sources:

NTIS	National Technical Information Service Springfield, Virginia 22151
NTC	National Translation Center of the John Crear Library 35 West 33rd Street Chicago, Illinois 61606
BISI	British Iron and Steel Industry Translation Service The Iron and Steel Institute 39 Victoria Street London, S.W. 1, England

1.6. Introduction References

[1] Butrymowicz, D. B., Manning, J. R., and Read, M. E., "Diffusion in Copper and Copper Alloys. Part I. Volume and Surface Self-Diffusion in Copper," J. Phys. Chem. Ref. Data **2** (3) 643–655 (1973).

[2] Butrymowicz, D. B., Manning, J. R., and Read, M. E., "Diffusion in Copper and Copper Alloys. Part II. Diffusion in Copper-Silver and Copper-Gold Systems," J. Phys. Chem. Ref. Data **3** (2) 527–602 (1974).

[3] Butrymowicz, D. B., Manning, J. R., and Read, M. E., "Diffusion in Copper and Copper Alloys, Part III. Diffusion in Systems Involving Elements of the Groups IA, IIA, IIIB, IVB, VB, VIB, and VIIB," J. Phys. Chem. Ref. Data **4** (1) 177–249 (1975).

[4] Butrymowicz, D. B., Manning, J. R., and Read, M. E., "Diffusion in Copper and Copper Alloys. Part IV. Diffusion in Systems Involving Elements of Group VIII," J. Phys. Chem. Ref. Data **5** (1) 103–200 (1976).

[5] Tomizuka, C. T., "Diffusion," Chapter 4.5 in *Solid State Physics*, Vol. 6, Part A, edited by K. Lark-Horowitz and V. A. Johnson (Academic Press, New York, 1959) pp. 364–373.

[6] Tomizuka, C. T., "Some Experimental Aspects of Diffusion in Metals," Adv. Mater. Res. **1**, 279–299 (1967).

[7] Lundy, T. S., "Volume Diffusion in Solids," Chapter 9A in *Techniques of Metals Research*, Vol. **4**, edited by R. F. Bunshah (Wiley-Interscience, New York, 1970) Part 2, *Physicochemical Measurements in Metals Research*, edited by R. A. Rapp, pp. 379–403.

[8] Adda, Y., and Philibert, J., *La Diffusion Dans Les Solides*, Vols. I and II (in French) (Presses Universitaires de France, Paris, 1966) 1268 pp.

[9] Gjostein, N. A., "Surface, Grain Boundary and Dislocation Pipe Diffusion," Chapter 9B in *Techniques of Metals Research*, Vol. 4, edited by R. F. Bunshah (Wiley-Interscience, New York, 1970) Part 2, *Physicochemical Measurements in Metals Research*, edited by R. A. Rapp, pp. 405–457.

[10] Manning, J. R., "Cross Terms in the Thermodynamic Diffusion Equations for Multicomponent Alloys," Metall. Trans. **1**, 499–505 (1970).

[11] See e.g., Manning, J. R., *Diffusion Kinetics for Atoms in Crystals* (D. Van Nostrand, Princeton, 1968) 257 pp.

[12] Barrer, R. M., *Diffusion in and through Solids* (Cambridge University Press, Cambridge, 1951) 464 pp.

[13] Jost, W., *Diffusion in Solids, Liquids, Gases* (Academic Press Inc., New York, 1952) 558 pp.

[14] Himmelsbach, C. J., and Brociner, G. E., *A Guide to Scientific and Technical Journals in Translation*, 2nd edition (Special Libraries Adsociation, New York, 1972) 49 pp.

2. Copper-Arsenic

2.1. As*→Cu

The value for the impurity-tracer diffusion coefficient of arsenic in copper most often quoted in the literature is found in the review paper of Lazarus (his ref. 104 in [1]). This reference [1] probably refers to the unpublished work of Tomizuka [2], who found that the diffusion of ^{76}As impurity in pure copper in an unspecified temperature range less than 300° C below the melting point could be expressed by the following:

$$D^{*}=D_0 \exp(-Q/RT)=0.12 \exp(-42\ \mathrm{kcal \cdot mol^{-1}}/RT)\ \mathrm{cm^2/s}.$$

More recently, Klotsman et al. [3] studied the diffusion of the tracer-impurity ^{73}As in polycrystalline copper in the temperature range 810–1075 °C. Analysis of their penetration plots yielded the coefficients (and their probable errors) listed in table 1. An Arrhenius plot of these data is shown in figure 1. The following Arrhenius equation results from the plot:

$$D^{*}=0.202^{+0.041}_{-0.034} \exp[-(42.13\pm0.44)\ \mathrm{kcal \cdot mol^{-1}}/RT]\ \mathrm{cm^2/s},$$

and is in good agreement with Tomizuka's unpublished work.

2.2. Cu-As Interdiffusion

Interdiffusion studies in the Cu-As system at 903 °C have been reported [4]. Pure copper was bonded to a Cu-As(2.72 at.%) alloy and the large-grained polycrystalline specimens were diffusion-annealed for 5, 20, and 80 hours. After diffusion, the couples were sectioned in a plane parallel to the direction of diffusion and the arsenic and copper concentrations were determined with an electron microprobe analyzer. Ziebold and Ogilvie's empirical method [5] of analysis was applied to the microprobe data. The interdiffusion coefficients were calculated following the method of Grube [6]. The linear probability plots gave diffusion coefficients that had a range $(2.47\text{–}3.85)\times10^{-9}$ cm^2/s. These results are in good agreement with the tracer-impurity results of Klotsman et al. [3]. Since the interdiffusion studies were carried out with dilute solid-solutions of arsenic in copper, the value of the diffusion coefficient of arsenic obtained should approach the value of the tracer-impurity coefficient.

2.3. Cu-As-Al

Ternary alloys of Cu-As-Al have been bonded to pure copper and interdiffused at 903 °C in one study [4]. The alloys contained 9.74–10.4 at.% aluminum and 1.32–1.60 at.% arsenic. After being diffused into pure copper for 5–80 hours, the concentration-penetration profiles of arsenic and aluminum were determined with an electron microprobe analyzer. It was found that when arsenic and aluminum were diffused in parallel with each other into pure copper, a case of "uphill" diffusion occurred. There was a build-up of arsenic at the interface of the diffusion couple. Additionally, both the arsenic and aluminum diffused much faster than when interdiffused into copper

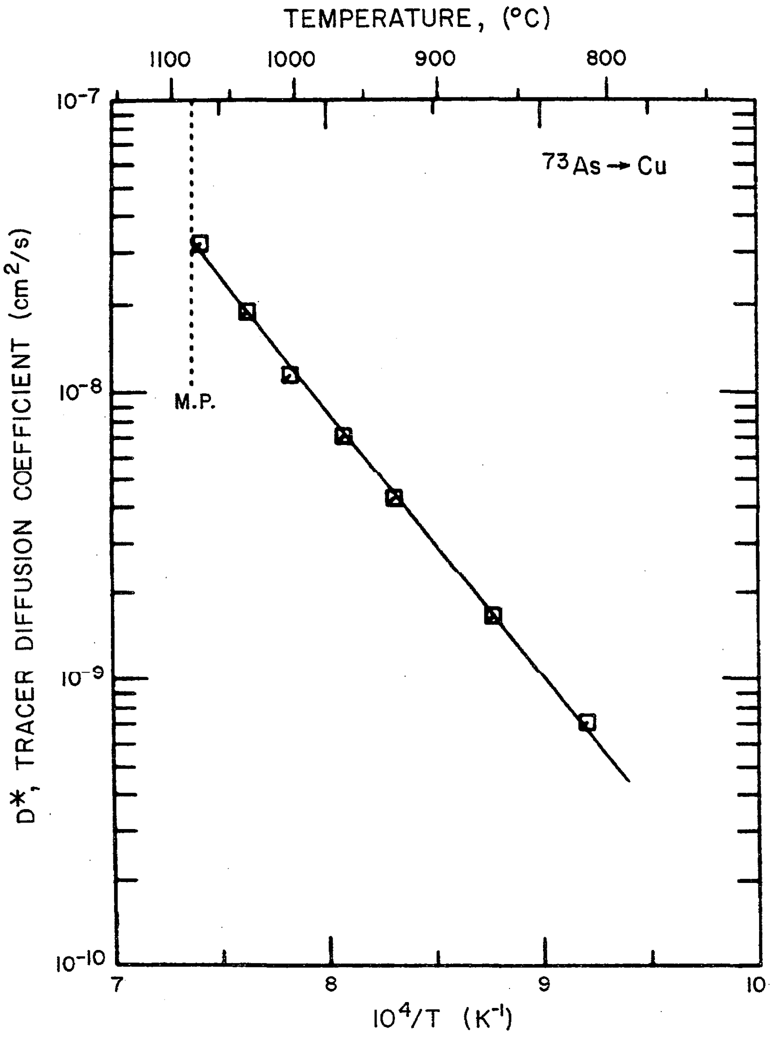

FIGURE 1. Tracer diffusion coefficients of ^{73}As in polycrystalline copper as a function of reciprocal absolute temperature.

Data from Klotsman et al. [3].

separately. An "average" diffusion coefficient for arsenic had a range $(3.97\text{–}5.80) \times 10^{-8}$ cm²/s, and for aluminum a range $(2.47\text{–}7.45) \times 10^{-9}$ cm²/s, at 903 °C. These values represent an "average" diffusion coefficient and may differ significantly from the true coefficient of interdiffusion.

The counterdiffusion of aluminum and arsenic in a copper matrix was also studied in the same reference [4]. In these experiments, alloys of Cu-Al(12.0 at.%) and Cu-As(2.72 at.%) were bonded to either side of a pure copper interlayer and interdiffused for 5, 20, and 80 hours at 903 °C. Electron microprobe analysis was employed to determine the aluminum and arsenic concentrations. A "band" of arsenic and aluminum, normal to the direction of counterdiffusion and migrating as a function of time, was detected with microprobe analysis and micrometallographically. These bands of Al-As "precipitates" reveal themselves as discontinuities in the concentration-penetration plots. Because of the inflections in the penetration plots, only "average diffusion coefficients" were calculated. This diffusion coefficient for arsenic had a range $(3.50\text{–}5.10) \times 10^{-9}$ cm²/s at 903 °C. It was concluded that aluminum and arsenic do not diffuse as a pair when diffusing in the presence of each other. Movement of the bands of aluminum and arsenic is believed to be rate-governed rather than quantity-governed.

Similar counterdiffusion studies were performed by Gerrard [7], and Gerrard et al. [8]. In these experiments, alloys of Cu-Al(8.4–11.4 at.%) were bonded to alloys of Cu-As($\approx$1.55 at.%), as well as across a pure-copper interlayer. After interdiffusion at 903 °C,

TABLE 1. Tracer diffusion coefficients of ^{73}As in copper. Data of Klotsman et al. [3].

T (°C)	D* (cm^2/s)
1075	$3.21\ (\pm 0.01) \times 10^{-8}$
1036	$1.89\ (\pm 0.01) \times 10^{-8}$
1002	$1.16\ (\pm 0.01) \times 10^{-8}$
964	$7.11\ (\pm 0.03) \times 10^{-9}$
929	$4.30\ (\pm 0.02) \times 10^{-9}$
866	$1.67\ (\pm 0.01) \times 10^{-9}$
813	$7.15\ (\pm 0.02) \times 10^{-10}$

the solute concentrations of arsenic and aluminum were determined by x-ray diffraction and wet chemical analysis. Aluminum-arsenic "precipitates" were found to exist as a metastable phase in the form of bands, normal to the direction of interdiffusion, which migrated as a function of time. Gerrard proposes a physical model and then uses it as a basis to derive a mathematical model which expresses the aluminum-arsenic band location as a function of time. These models allow one to calculate the diffusivity of aluminum and arsenic from observed band migration. The diffusion coefficients arrived at from this indirect measurement are in fair agreement with the direct and more reliable measurements of Butrymowicz [4].

2.4. Cu-As-Ga

An interdiffusion study where gallium and arsenic were "counterdiffused" in a copper matrix was reported by Kelly [9]. This counterdiffusion experiment is similar to those performed by Butrymowicz [4], Gerrard [7], Gerrard et al. [8], Chenot [10], and Meiser [11], differing only in that alloys of Cu-Ga(12.9 at.%) were bonded to alloys of Cu-As(1.3 at.%). All alloys are single phase (α-solid solutions). During the diffusion anneals at 900 °C, the counterdiffusing species, gallium and arsenic, interact and accumulate in visible bands of "precipitates," normal to the direction of diffusion and parallel to the bonded interface. A mathematical model based on the maximum rate of change in concentration of the diffusants (Ga and As) was derived. A correlation of the micro-metallographically visible bands of Ga-As, based on the strain imparted to the copper lattice by the interaction of the two diffusants, is given. No interdiffusion coefficients were calculated, although x-ray back-reflection and powder diffraction patterns were taken to determine the gallium and arsenic penetration curves.

The impurity diffusion of copper into the semiconducting compound, GaAs, has received much attention because of its obvious technological importance. A number of excellent reviews on diffusion in GaAs have been published [12–21], and thus the discussion here will be brief.

All of the investigations have reported copper to be a very fast diffusant in GaAs [22–35]. Fuller and Whelan [22] were the first to show that copper diffuses rapidly into GaAs and propose a interstitial-substitutional role for copper in the diffusion process. They electrodeposited radioactive ^{64}Cu onto their GaAs specimens and diffused them over a temperature range 700–1200 °C (±3 °C). Standard counting techniques were used to determine the copper concentrations introduced at various temperatures. Autoradiography was employed to examine transient behaviors. Irregular concentration profiles were found, indicating both a rapidly, as well as discontinuously, changing diffusion coefficient. Although ideal conditions required for the error-function solution are not fulfilled, single error-function curves can be fitted to the curves on either side of the discontinuities (see figure 2), and an apparent value of D is calculated. These apparent diffusion coefficients are:

$$\text{at } 1003\ ^\circ\text{C},\ D_{\text{apparent}}=(0.83\text{–}1.4)\times 10^{-5}\ \text{cm}^2/\text{s};$$

$$\text{at } 1110\ ^\circ\text{C},\ D_{\text{apparent}}=(2.1\text{–}3.1)\times 10^{-5}\ \text{cm}^2/\text{s}.$$

In addition to the above coefficients, the autoradiographs indicate that copper enters the crystal interstitially at a very high rate (the apparent diffusion coefficient is $\approx 10^{-4}$ cm^2/s at 1100 °C). This first study of copper diffusion in GaAs yielded some qualitative results which pointed out the rapid interstitial behavior of copper in the compound.

Fuller and Wolfstirn [23, 24] looked at the interaction of divacancies with defects and impurities during the diffusion of copper in GaAs.

Hall and Racette [25–27] in a detailed study measured the solubility, diffusion, and drift of copper in the extrinsic, p-type GaAs. Purer materials were employed, and the temperature range was extended lower than that of earlier studies. Additionally, their experimental conditions were designed to allow for the measurement of the diffusion coefficient of only the interstitial copper in the GaAs lattice. After the radioactive ^{64}Cu was plated and diffused into the GaAs, the specimens were sectioned and autoradiographs made. The copper penetration was determined by densitometry. The interstitial copper diffusion coefficient was obtained from the densitometer data utilizing the methods of Olson and Schultz [36]. A plot of the tracer impurity diffusion coefficients for interstitial

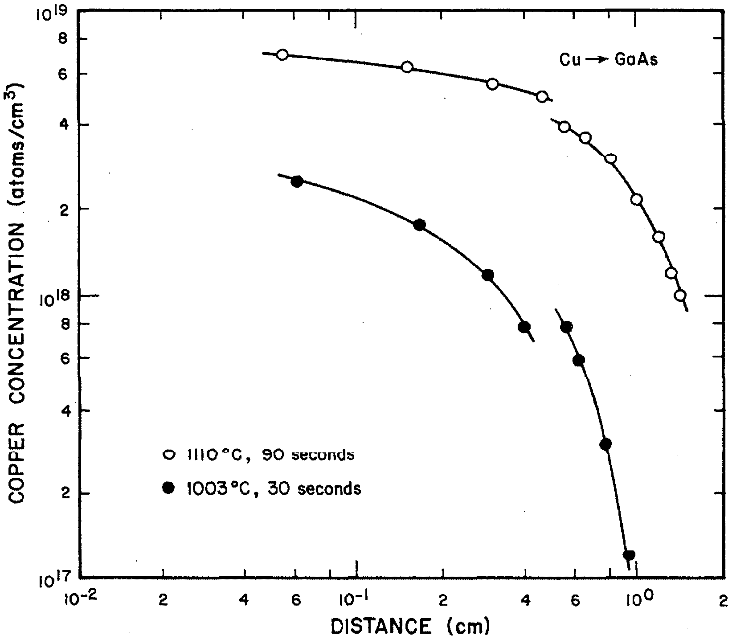

FIGURE 2. The change in copper concentration versus diffusion distance on a log-log plot.

Apparent diffusion coefficients (cm²/s) are indicated. Data from Fuller and Whelan [22].

copper in GaAs is shown in figure 3 and can be calculated from the expression:

$$D^{\text{interstitial}}_{\text{Cu}^{+}\rightarrow\text{GaAs}}=0.030\ \exp(-0.53\ \text{eV}/kT)\ \text{cm}^2/\text{s}.$$

Ion-drift experiments performed in an applied electric field also allowed diffusion coefficients to be calculated. The calculated values from the Einstein relation are in agreement with their other determinations (see table 2).

TABLE 2. Copper diffusion coefficients determined from drift of copper in extrinsic *p*-type GaAs. Data of Hall et al. [26].

T (°C)	Drift Distance (mm)	Electric Field (V/cm)	D (cm²/s)
255	5	2.00	1.8×10^{-7}
220	5	1.77	1.6×10^{-7}
200	0.56	1.08	3.7×10^{-8}
195	0.64	1.45	3.1×10^{-8}

Although the complete data of Hall and Racette show considerable scatter, the results include experimental points taken while measuring techniques were still being improved, as well as points taken to check the measuring techniques. Additionally, the emphasis was placed upon measuring diffusion in several different ways (out-diffusion, ion-drift, etc.) to avoid possible misinterpretation of the data, rather than achieving the greatest possible accuracy through refinement of a particular experimental method. The pre-exponential, D_0, is probably correct within a factor of 3, and the activation energy, Q, for diffusion is 0.53 ± 0.05 eV.

Kendall [13, 37] in looking at Hall and Racette's results proposed an interstitial-substitutional mechanism for the impurity diffusion of copper in GaAs. An "interstitial-substitutional" diffusion coefficient can be calculated from Kendall's model and is shown in figure 4. The impurity diffusion coefficient of copper in GaAs can thus be expressed as:

$$D^{\text{impurity}}_{\text{Cu}\rightarrow\text{GaAs}}=1.0\times10^{-3}\ \exp\ (-0.53\ \text{eV}/kT)\ \text{cm}^2/\text{s},$$

for an interstitial-substitutional mechanism. The results of Kendall's calculations (using Hall and Racette's data) are in good agreement with Fuller's [22] values at the higher temperatures.

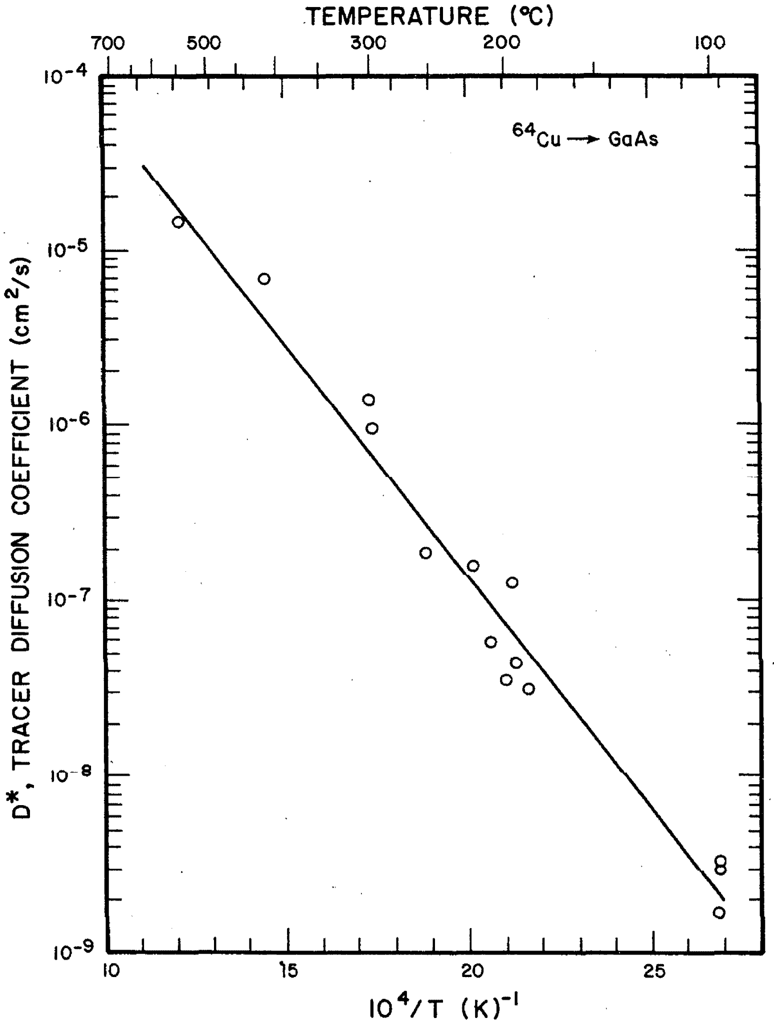

FIGURE 3. Tracer diffusion coefficients of interstitial ^{64}Cu in extrinsic p-type GaAs as a function of reciprocal absolute temperature.

Data from Hall and Racette [26].

Hall and Racette's experiments with copper diffusion into extrinsic n-type GaAs yielded much different results. Cooper diffusion was much faster near the surface, with the rate of diffusion becoming much slower in the interior of the specimen. Larrabee and Osborne [28] looked at this behavior in more detail in their study of radioactive ^{64}Cu diffusion into n-type GaAs. In their studies at 815 °C, they found diffusion profiles that had a slowly diffusing branch near the surface, and a faster diffusing branch deeper in the specimen. An effective diffusion coefficient for the ^{64}Cu impurities has been calculated for both branches of the profile [13]. In the slowly diffusing area near the surface, $D_{\text{effective}}$ varies from $(2\text{–}5)\times 10^{-11}$ cm^2/s. More deeply, the effective diffusion coefficient varies from $(1\text{–}5)\times 10^{-7}$ cm^2/s.

Boltaks and Dzhafarov [29] observed the same behavior (see figure 5) when they diffused radioactive ^{64}Cu into n-type GaAs (electron concentration$=3\times 10^{17}$/cm^3; electron mobility$=3400$ cm^2/V·s). Their experiments were limited to only one temperature, 940 °C. Unfortunately, their sectioning techniques and contact autoradiography methods allowed them to only estimate the copper impurity diffusion coefficient ($\approx 10^{-6}$ cm^2/s at 940 °C) for the deeper branch of the concentration-distribution curve.

Room temperature experiments utilizing radioactive ^{64}Cu yielded diffusion coefficients of the order of 10^{-10} cm^2/s [38]. Although a novel experimental technique was employed, the results are in agreement with the above-mentioned experiments of Hall and Racette [25–27].

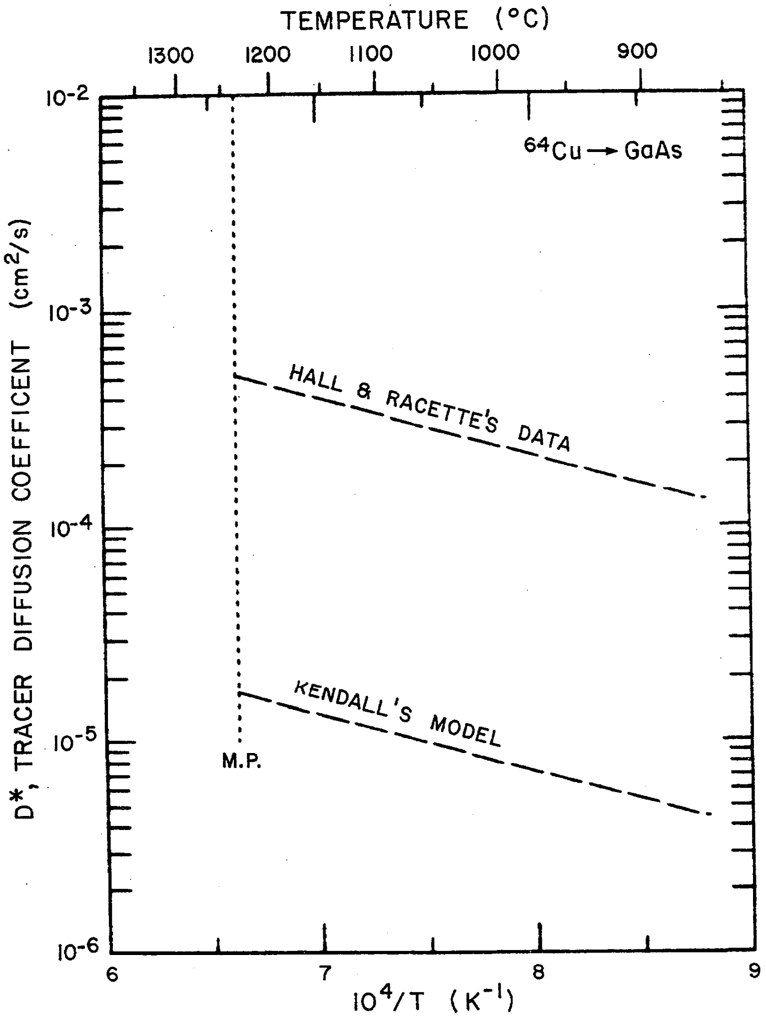

FIGURE 4. Tracer diffusion coefficients of ^{64}Cu in GaAs at low copper concentration as a function of reciprocal absolute temperature.

The upper curve is an extrapolation of Hall and Racette's data [26]. The lower curve is the result of Kendall [13] employing his model to Hall and Racette's data.

It is interesting to note that Larrabee and Osborne [28] recorded a depression in the ^{64}Cu diffusion profiles in the vicinity of a *p-n* junction when the copper was diffused simultaneously with zinc and manganese (e.g., see figure 6). The magnitude of the depression and the zone over which it extended varied with the diffusion conditions of time and temperature. This pronounced minimum in the copper diffusion profile and the subsequent uphill diffusion has been explained by Kendall [13, 37, 39] in terms of an interstitial-substitutional mechanism similar to that proposed for the diffusion of copper in germanium [40].

Ultrasonic techniques have been utilized to measure the impurity diffusion coefficient of copper in undoped *n*-type GaAs [33, 34]. A relationship is developed between the thickness of the diffusion layer, the value of the "effective" or "apparent" diffusion coefficient on the impurity time of diffusion annealing, and the resonance frequency. It is then possible to measure the diffusion coefficient of a compensating impurity (in this case, Cu) in piezoelectric semiconductor materials through the determination of the frequency characteristics of electroacoustic transducers with a diffused layer. The investigations were directed towards the determination of an effective diffusion coefficient for substitutional copper atoms in undoped *n*-type GaAs. Figure 7 illustrates the dependence of this effective diffusion coefficient (at 500 °C) on the arsenic composition of the crystal-growing melt. The temperature dependence of the effective diffusion coefficient of substitutional copper atoms in GaAs is shown in figure 8.

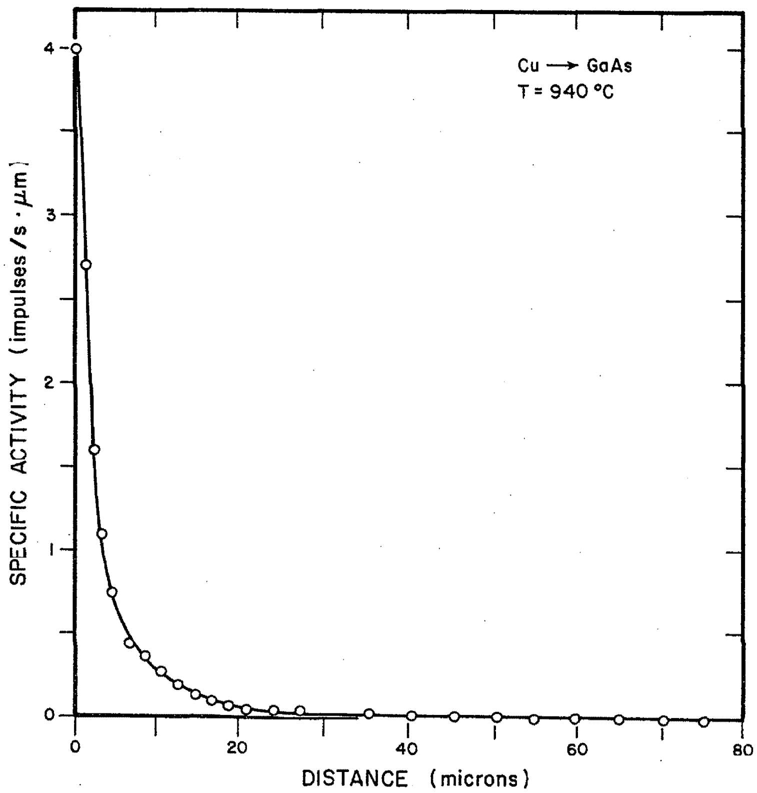

FIGURE 5. Copper distribution in *n*-type GaAs at 940 °C.

Data from Boltaks and Dzhafarov [29].

These results, obtained through a rather indirect measurement technique, are in poor agreement with the earlier-mentioned results obtained by the more direct methods employing radioactive tracers. The disagreement probably stems from the inherent difficulties of the non-direct measurement methods employed. It is also not apparent how the authors sorted out the complex processes occurring during diffusion to obtain an effective diffusion coefficient for purely substitutional copper. Results obtained from the radioactive tracer studies should be definitely favored over the measurement of transducer frequency characteristics.

The effect of dislocations of the diffusion behavior of copper in GaAs has been reported [30]. It was shown quantitatively from photoluminescence and conductivity measurements that dislocations act as sources and sinks, respectively, for the diffusion and precipitation of copper in GaAs. At 600 °C, a diffusion coefficient of 5×10^{-10} cm^2/s was determined. The results indicate that copper diffuses much faster along dislocations than in dislocation-free bulk material.

2.5. Cu-As-In

The impurity diffusion of electrodeposited, radioactive ^{64}Cu into the semiconducting compound InAs has been the subject of several investigations [41, 42].

Fuller and Wolfstirn's investigation [41] extended over the temperature range 248–506 °C. Boltaks et al. [42] performed their experiments over a temperature range 525–890 °C. Despite these markedly different temperature ranges, the results agree concerning the value of the activation energy. However, they differ in the value of the pre-exponential term of the Arrhenius equation. Both experiments appear to have been carefully performed and the differences in results can probably be ascribed to the purity of the InAs used, as well as the inherent deficiencies in the two different techniques employed to obtain the copper concentration-penetration profiles and impurity diffusion coefficient calculations.

Fuller and Wolfstirn [41] used an InAs crystal which contained less than 1.0 atomic part per million of carbon, oxygen, and nitrogen; sulfur, selenium, tellurium and all metallic impurities were less than 0.5 atomic part per million. The InAs crystal also had

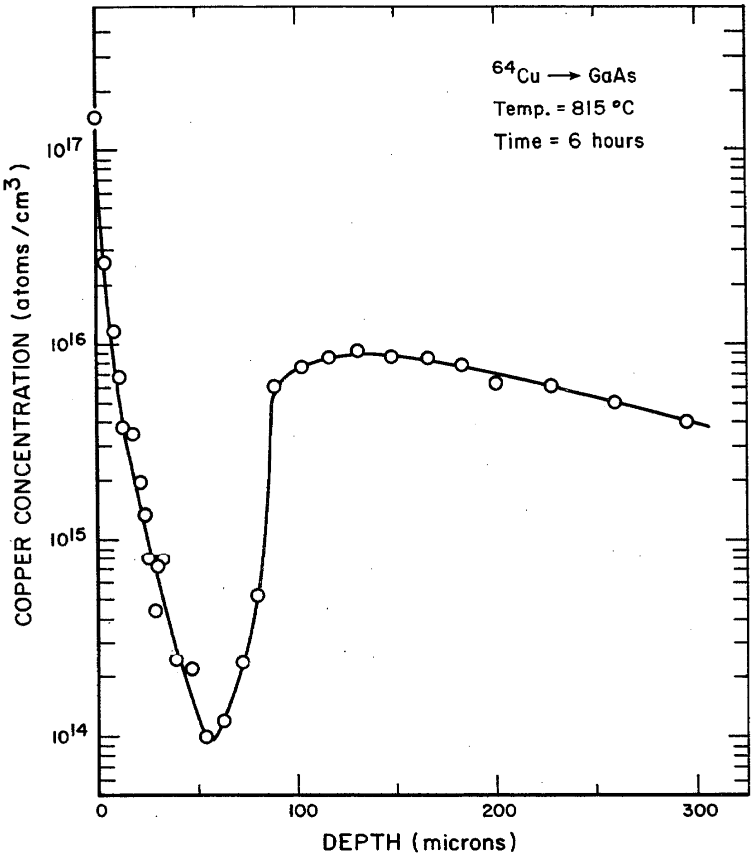

FIGURE 6. Typical distribution of ^{64}Cu in n-type GaAs when diffused with Mn at 815 °C for 6 h.

Data from Larrabee and Osborne [28].

the following electrical properties: an electron concentration of $(1.6\text{–}2.0)\times10^{16}/cm^3$ (at 298 K), and $(1.4\text{–}1.8)\times10^{6}/cm^3$ (at 77 K); an electron mobility of 27,000 (at 298 K) and 58,000 (at 77 K) $cm^2/V\cdot s$. The density of dislocations was $100/cm^2$.

Boltaks et al. [42] investigated single crystals of unspecified purity which possessed the following electrical properties: electron concentration of $(2\text{–}60)\times10^{16}/cm^3$; electron mobility of 14,000 25,000 $cm^2/V\cdot s$ The etch pit density was approximately $10^3/cm^2$. Boltaks et al. diffusion-annealed their specimens in sealed quartz ampoules filled with argon, whereas Fuller and Wolfstirn carried out their diffusions in air.

After the diffusion anneals of Fuller and Wolfstirn, the copper-penetration profiles were determined from lapping the surfaces of the diffused specimens parallel to the diffusion plane and counting the radioactivities of the grindings. The diffusion coefficient was calculated (with a "constant-surface concentration" boundary condition) from a graphical procedure suggested by Bardeen and described by Fuller and Ditzenberger [43]. This procedure is employed when data points are rather far apart because of the short half-life of the radioactive isotope (in this case, ^{64}Cu). Figure 9 shows a semi-log plot of the diffusion coefficient calculated from this procedure versus reciprocal absolute temperature. For the temperature range in question, the diffusion of copper in the semiconducting compound InAs can be expressed by the following Arrhenius relation:

$$D^{\text{impurity}}_{\text{Cu}\to\text{InAs}}=3.55\times10^{-3}\exp\left[-0.52\ \text{eV}/kT\right]\ \text{cm}^2/\text{s}.$$

In the high-temperature studies of Boltaks et al., the copper concentrations were determined by autoradiography and sectioning as described by Reiss et al. [44]. The resulting diffusion coefficients are plotted in figure 10. The temperature dependence of the impurity diffusion coefficient for these results can be expressed as:

$$D^{\text{impurity}}_{\text{Cu}\to\text{InAs}}=2.2\times10^{-2}\exp\left[-(0.54\pm0.08)\ \text{eV}/kT\right]\ \text{cm}^2/\text{s}.$$

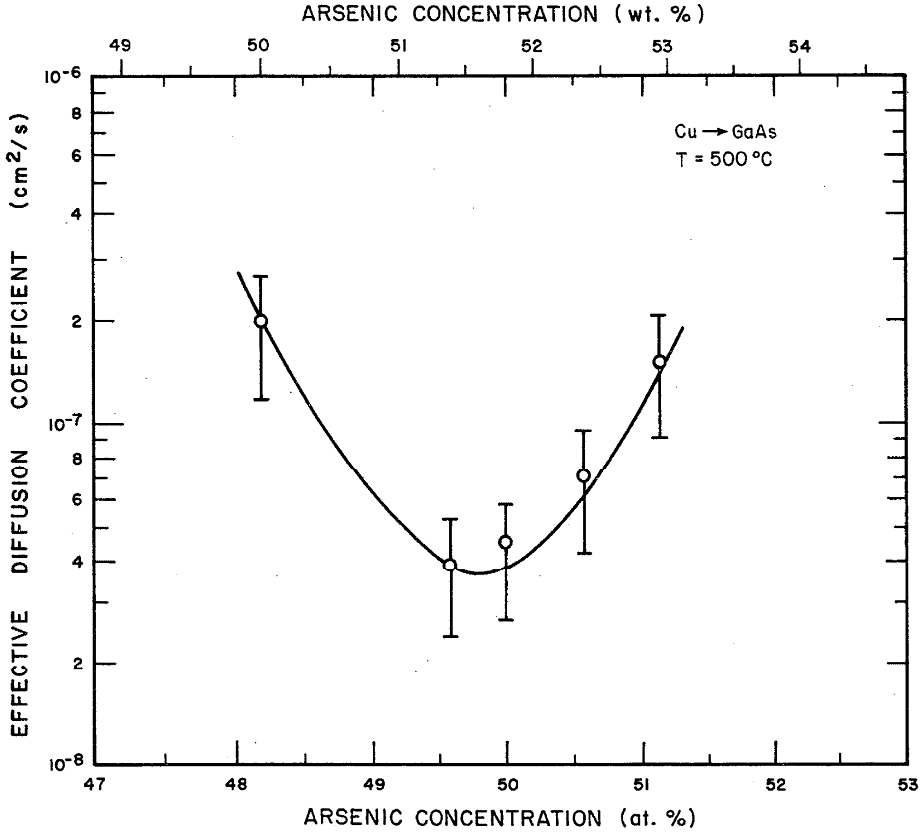

FIGURE 7. Effective diffusion coefficients of substitutional copper in undoped *n*-type GaAs as a function of arsenic composition of the crystal-growing melt at 500 °C.

Data from Vasil'ev et al. [34].

The entropy and enthalpy terms in the above equation indicate that copper in InAs is essentially a pure interstitial with diffusion apparently proceeding with little or no participation of vacancies. Some of Fuller and Wolfstirn's observations indicate that this may be true down to as low a temperature as 200 °C.

This interstitial impurity diffusion of copper is typical of the rapid diffusion observed for the noble metals in III-V compounds and is similar to their diffusion in elemental semiconductors (e.g., Ge and Si).

2.6. Cu-As-Ni

The preliminary results of a study of the effect of arsenic (2.7 at.%) on the diffusion of copper in nickel single crystals has been reported [45, 46]. High-purity copper (impurity level less than 10 ppm) was vacuum evaporated onto nickel (impurity level less than 10 ppm) single crystals containing 10^3–10^4 dislocations per square centimeter. The gradient of copper concentration in nickel was measured with an electron microprobe analyzer. The only result available showed that arsenic increased the impurity diffusion of copper (see figure 11).

2.7. Cu-As-Se

A very qualitative study has been made on the diffusion and reactivity of copper on thin films of amorphous arsenic triselenide (As_2Se_3) [47]. Thin films of copper (several hundred angstroms thick) were evaporated onto amorphous films (about 500 Å thick) of As_2Se_3. Diffusion annealing at 60 °C for periods of up to 26 days indicated that copper was very mobile in the As_2Se_3, reacting and forming precipitates in the film.

2.8. Cu-As-Zn

Accary [48–51] investigated the effect of arsenic impurities on the rate of diffusion of zinc in α-brasses. Arsenic impurities (up to 0.25 at.%) were added to brasses (70 wt% Cu–30 wt% Zn), and the rates of evaporation and/or condensation were measured in the temperature range 650–950 °C. The diffusion coefficients were calculated from weight changes of the test specimens. Micrometallographic examination

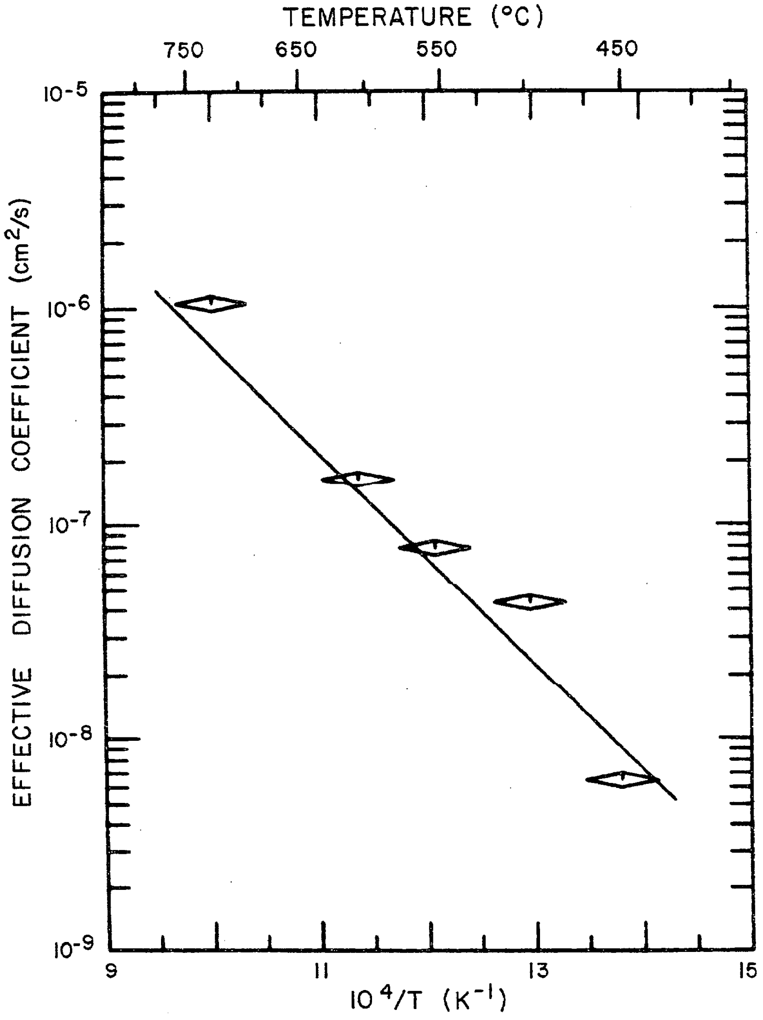

FIGURE 8. Effective diffusion coefficients of substitutional copper in undoped *n*-type GaAs as a function of reciprocal absolute temperature from Vasil'ev et al. [34].

The displayed points represent an estimation of the actual data from the authors' published graph. Due to the unusual scale of the published graph, estimates of the temperature coordinates exhibit a large uncertainty. The size of the data points represent the approximate uncertainty in each direction of the interpolation.

supplemented the weight-change measurements. Arsenic impurities (up to 0.25 at.%) were found to be responsible for a marked increase in the rate of zinc diffusion. A typical illustration of this effect is shown in figure 12.

2.9. Cu-As-X

The impurity diffusion of radioactive copper in both the crystalline and glassy modifications of $CdGeAs_2$ has been reported [52, 53]. The temperature range of the diffusion anneal in the non-crystalline modification was 200–400 °C and 300–600 °C in the unoriented single crystals. Copper diffusion in this crystalline semiconductor exhibited a linear temperature dependence which was described by the following Arrhenius equation:

$$D^*_{\mathrm{Cu}}=1.6\times10^{-2}\exp(-1.05\ \mathrm{eV}/kT)\ \mathrm{cm}^2/\mathrm{s}.$$

Diffusion in the glassy semiconductor is characterized by an activitation energy of 0.75 eV and a pre-exponential of 3.1×10^{-3} cm²/s.

It is difficult to assess the reliability of the above data since experimental details were extremely sketchy and no errors with regard to precision or accuracy were reported (although it was stated that all the copper concentration profiles were either exponential or satisfied the complementary error-function). No

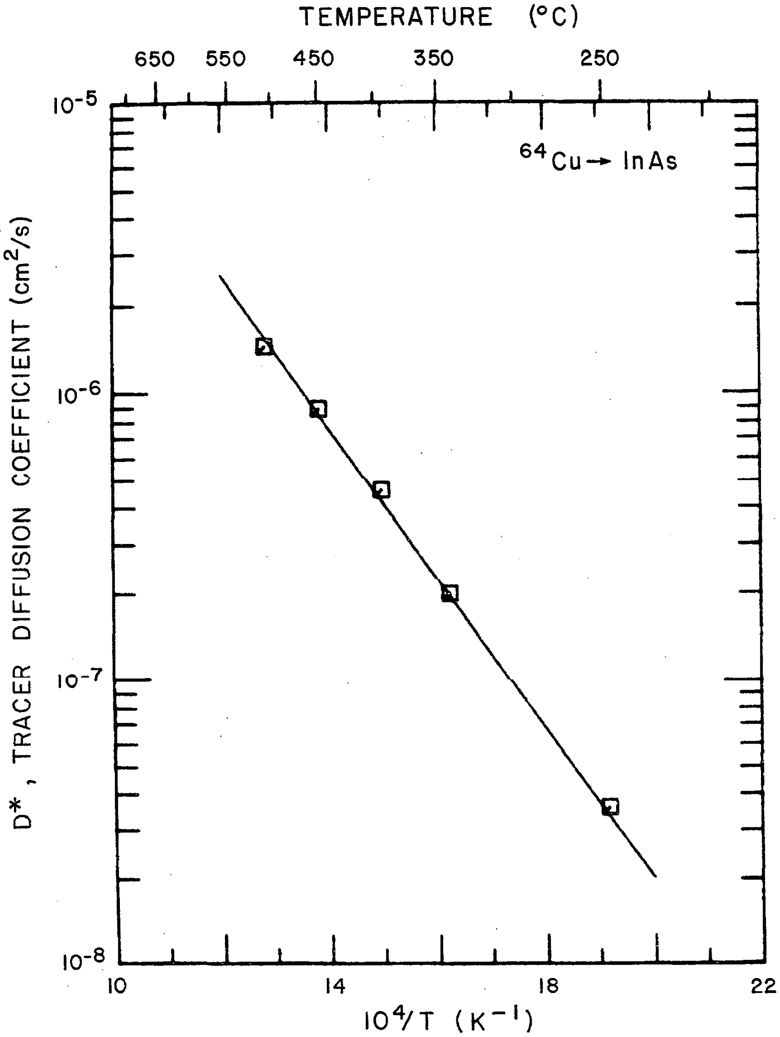

FIGURE 9. Tracer diffusion coefficients of ^{64}Cu in InAs at low temperatures as a function of reciprocal absolute temperature.

Data from Fuller and Wolfstirn [41].

attempt was made to sort out the rates of copper diffusion along the different crystallographic directions since gold and cadmium did not have an orientation dependence in some preliminary studies by the same authors.

The authors of the paper did note that copper diffusing in other semiconductors (Si, Ge, PbSe, InSb, etc.) had diffusion coefficients reasonably close to those determined in this ternary semiconductor. Activation energies, though, did differ considerably, being less than that for diffusion in $CdGeAs_2$. Similar behavior was exhibited by the other noble metals, *Ag* and *Au*.

2.10. Grain-Boundary Diffusion

The grain-boundary diffusion of ^{73}As in copper was investigated by Klotsman et al. [3] in the temperature range 340–550 ° C. Applying Fisher's analysis [54] to their data results in the following expression for the grain-boundary diffusion coefficient of ^{73}As in copper:

$$\delta \cdot D_{gb} = (7.9^{+8.5}_{-4.1}) \times 10^{-10} \exp[-(12.35 \pm 0.97)\ \mathrm{kcal \cdot mol^{-1}}/RT]\ \mathrm{cm^3/s},$$

where δ=grain-boundary width.

The data have a fair amount of scatter and this is reflected in the error limits in the above equation.

2.11. Electromigration

The effect of an applied dc electric field on the impurity diffusion of copper ions in GaAs has been reported [29]. A thin layer of radioactive ^{64}Cu was electrodeposited onto single crystals of *n*-type (electron

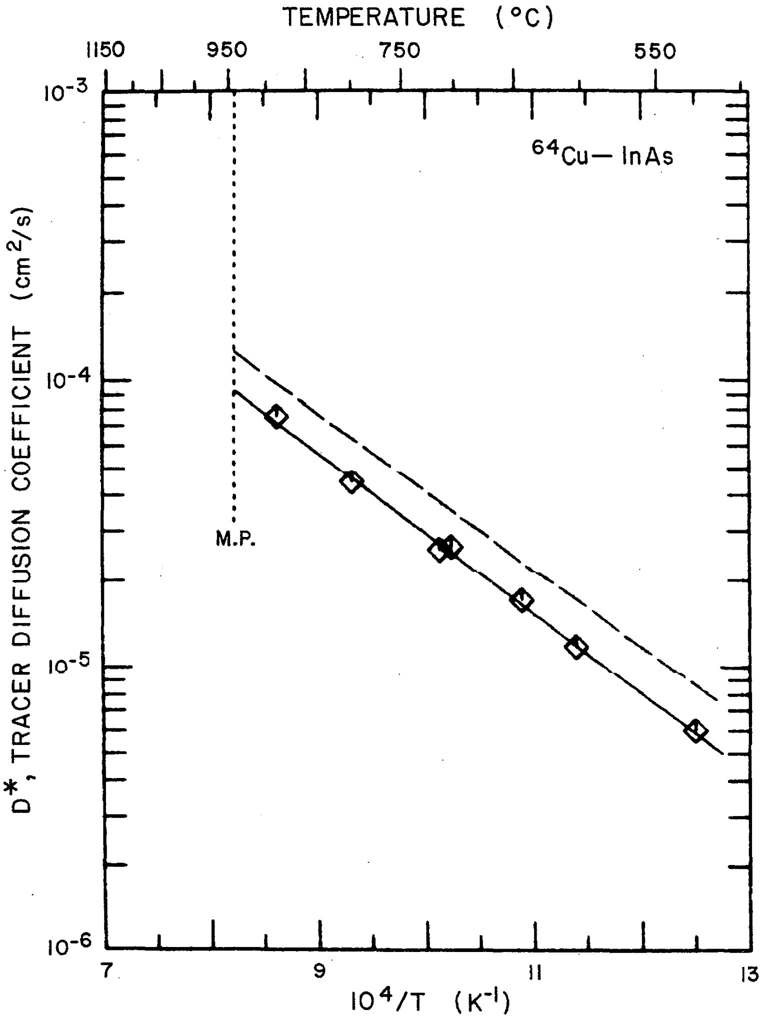

FIGURE 10. Tracer diffusion coefficients of ^{64}Cu in InAs at high temperatures as a function of reciprocal absolute temperature from the data of Boltaks et al. [42].

The dashed line is Boltaks' stated line with $D_0=2.2\times10^{-2}$ cm^2/s, and $Q=0.54\pm0.08$ eV. The solid line is a least-squares line with $D_0=1.96\times10^{-2}$ cm^2/s, and $Q=0.56$ eV.

concentration$=3\times10^{17}$/cm^3; electron mobility$=3400$ cm^2/V·s) and p-type (copper concentrations of $1-5\times10^{18}$/cm^3) GaAs. Electromigration took place over the temperature range 820–1000 °C with current densities of 55–97 A/cm^2 for 3–17 minutes. The electric field was the source of heating. The copper distribution within the GaAs was determined from a contact radiography method described by Boltaks [15]. A typical copper distribution curve is shown in figure 13. The asymmetry of the curve indicates that the predominant migration of the copper is towards the cathode in GaAs. The effective mobilities and the effective charge calculated for the experimental results using n-type GaAs are listed in table 3. The results obtained with heavily-doped p-type GaAs showed that the radioactive copper migrated in the form of positive ions as in the case of n-type GaAs, but the experimentally measured charge of the copper ions was close to $+1$.

The results obtained indicate that the copper impurities diffuse mainly interstitially.

Photoluminescence spectra have been taken from samples of copper-diffused GaAs (doped with zinc) [35, 55–57]. These spectra have been analyzed to obtain the kinetics and rate of defect formation during copper diffusion in GaAs.

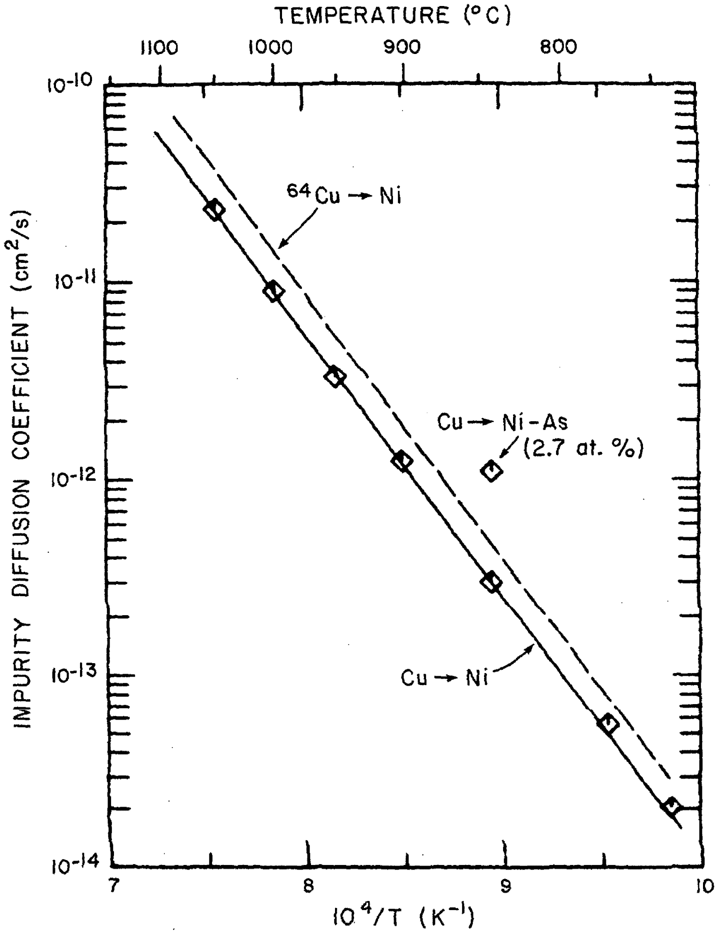

FIGURE 11. Impurity diffusion coefficients of copper in nickel and Ni-As(2.7 at .%) as a function of reciprocal absolute temperature from the data of Helfmeier et al. [45, 46].

Shown for comparison is the Arrhenius equation of Monma et al. extrapolated to these lower temperatures.

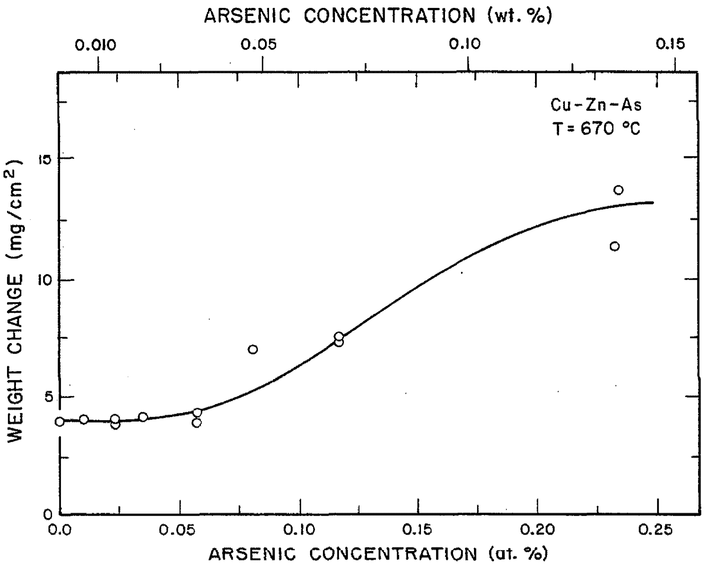

FIGURE 12. Weight changes of Cu-Zn(70–30) alloys containing arsenic as a function of arsenic concentration at 670 °C.

Zinc was dynamically evaporated. Data from Accary [48, 49].

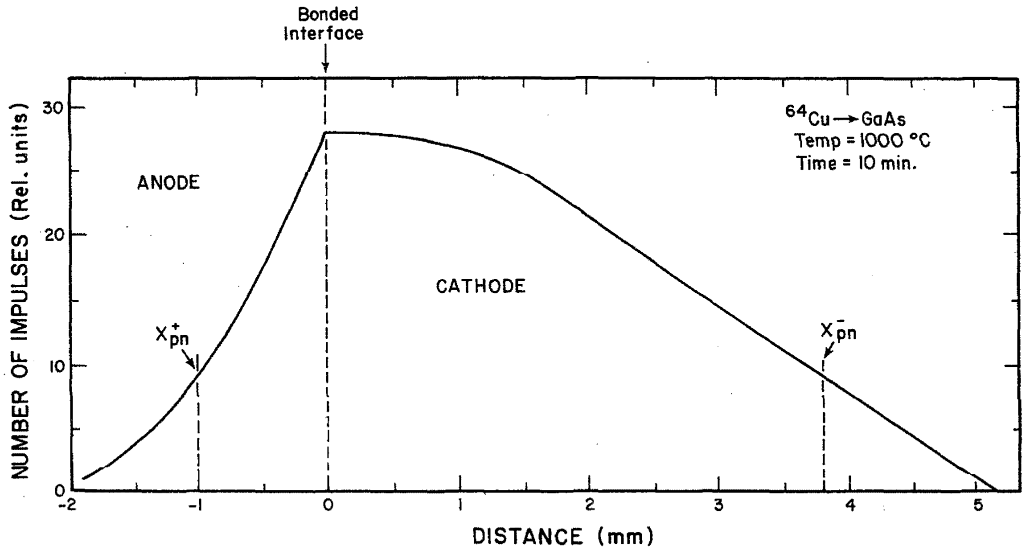

FIGURE 13. Distribution of ^{64}Cu ions in single-crystal *n*-type GaAs caused by application of a dc electric field at 1000 °C for 11 minutes.

Data from Boltaks and Dzhafarov [29].

TABLE 3. Electromigration of copper in GaAs. Data of Boltaks et al. [29].

T (°C)	t (s)	μ_{eff} (cm^2/V·s)	q_{eff}
1000	660	8.5×10^{-5}	0.3
950	480	9.9×10^{-5}	0.4
930	135	7.4×10^{-5}	0.4
850	1020	4.9×10^{-5}	-
820	720	9.8×10^{-6}	0.6

q_{eff} is the experimentally measured effective ion charge

μ_{eff} is the effective mobility

2.12. Cu-As References

[1] Lazarus, D., "Diffusion in Metals," in *Solid State Physics*, Vol. 10, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960) pp. 71–126.

[2] Nachtrieb, N. H., Tomizuka, C. T., and Schultz, L. G., Univ. Chicago, *Point Imperfections in Metals by Conductivity and Diffusion Measurements*, Final Report, Part 2, Prepared for the Office of Scientific Research, Air Research and Development Command, Contract No. AF18(600)–1489 (1960) pp. 2.1–2.15 [also available from NTIS as AD 232543].

[3] Klotsman, S. M., Rabovskiy, Ya. A., Talinskiy, V. K., and Timofeyev, A. N., "Impurity Diffusion in Polycrystalline Copper. II. Diffusion of Arsenic," (in Russian) Fiz. Met. Metalloved. **29** (4) 803–806 (1970) [Phys. Met. Metallogr. **29** (4) 127–131 (1970)].

[4] Butrymowicz, D. B., *Mechanism of Counterdiffusion in the Copper-Aluminum-Arsenic System: The Determination of Diffusion Coefficients and Concentration Profiles of Aluminum and Arsenic in the Neighborhood of Aluminum Arsenide Precipitates*, Ph.D. Thesis, Univ. Cincinnati (1965) 168 pp.

[5] Ziebold, T. O., and Ogilvie, R. E., "An Empirical Method for Electron Microanalysis," Anal. Chem. **36**, 322–327 (1964).

[6] Grube, G., and Jedele, A., "The Diffusion of Metals in the Solid State: Comm. No. 5, Diffusion and Corrosion of Copper-Nickel Alloys," (in German) Z. Elektrochem. **38**, 799–807 (1932) [translation available from NTC as TT 70–57875].

[7] Gerrard, J. E., *Multicomponent Diffusion and Precipitation in Metallic Systems*, Ph.D. Thesis, Univ. Cincinnati (1961) 76 pp.

[8] Gerrard, J. E., Hoch, M., and Meeks, F. R., "Counterdiffusion of Aluminum and Arsenic in Copper," Acta Metall. **10**, 751–758 (1962).

[9] Kelly, D. P., *A Study of Counterdiffusion in Copper Alloys*, Ph.D. Thesis, Univ. Cincinnati (1962) 48 pp.

[10] Chenot, C. F., *Diffusion-Controlled Periodic Precipitation of GaAs in Ag*, Ph.D. Thesis, Univ. Cincinnati (1964) 90 pp.

[11] Meiser, J. H., *Counterdiffusion of Aluminum and Arsenic in Iron*, Ph.D. Thesis, Univ. Cincinnati (1966) 67 pp.

[12] Weisberg, L. R., Radio Corporation of America, Princeton, N.J., *Synthesis and Characterization of Electronically Active Materials*, Prepared for the Dept. of Defense, Advanced Research Projects Agency, Materials Sciences Office, Technical Report No. 1, ARPA No. 446, Contract No. SD–182 (1964) pp. 27–42.

[13] Kendall, D. L., "Diffusion," Chapter 3 in *Semiconductors and Semimetals*, Vol. 4, edited by R. K. Willardson and A. C. Beer (Academic Press, New York, 1968) pp. 163–259.

[14] Weisberg, L. R., "Diffusion in GaAs," Trans Metall. Soc. AIME (Am. Inst. Min. Metall. Pet. Eng.) **230**, 291–296 (1964).

[15] Boltaks, B. I., in *Diffuziya v Poluprovodnikakh*, (in Russian) (Gosudarstvenno Izdatel'stvo Fiz.-Matematicheskoi Literatury, 1961) 462 pp. [*Diffusion in Semiconductors*, Chapter 10, edited by H. V. Goldsmid (Academic Press, New York, 1963) pp. 312–313].

[16] Sharma, B. L., *Diffusion in Semiconductors* (Trans Tech Publications, Clausthal-Zellerfeld, Germany, 1970), 200 pp.

[17] Hagel, W. C., "Diffusion," Chapter 20 in *Intermetallic Compounds*, edited by J. H. Westbrook (John Wiley & Sons, Inc., New York, 1967) pp. 377–404.

[18] Yarbrough, D. W., "Status of Diffusion Data in Binary Compound Semiconductors," Solid State Technol. **11**, 23–54 (1968).

[19] Yarbrough, D. W., U.S. Army Electronics Command, Fort Monmouth, N.J., *Status of Diffusion Data for Binary Compound Semiconductors*, Technical Report ECOM–2942 (1968) 58 pp. [also available from NTIS as AD 67004].

[20] Madelung, O., Chapter 5 in *Physics of III–V Compounds*, translated by D. Meyerhofer (John Wiley & Sons, Inc., New York, 1964).

[21] Cunnell, F. A., Edmond, J., and Harding, W., "Technology of Gallium Arsenide," Solid-State Electron. **1**, 97–106 (1960).

[22] Fuller, C. S., and Whelan, J. M., "Diffusion, Solubility, and Electrical Behavior in Gallium Arsenide," J. Phys. Chem. Solids **6**, 173–177 (1958).

[23] Fuller, C. S., and Wolfstirn, K. B., "Evidence for Divacancy Reaction in GaAs During Cu Diffusion," Solid State Commun. **2**, 87–90 (1964).

[24] Fuller, C. S., and Wolfstirn, K. B., "Further Investigation of 'Divacancy Reaction' During Cu Diffusion in GaAs," Solid State Commun. **2**, 277–280 (1964).

[25] Hall, R. N., and Racette, J. H., "Behavior of Cu in Ge, Si, and GaAs," Bull. Am. Phys. Soc. **7**, p. 234 (1962).

[26] Hall, R. N., and Racette, J. H., "Diffusion and Solubility of Copper in Extrinsic and Intrinsic Germanium Silicon, and Gallium Arsenide," J. Appl. Phys. **35**, 379–397 (1964).

[27] Hall, R. N., General Electric Co., Schenectady, N.Y., *Applications of Tunneling to Active Diodes*, Prepared for Air Force Cambridge Research Labs., Office of Aerospace Research, Scientific Report No. 7A, AFCRL–62–87, Contract No. AF19 (604)–6623 (1962) 45 pp. [also available from NTIS as AD 274391].

[28] Larrabee, G. B., and Osborne, J. F., "Anomalous Behavior of Copper During Acceptor Diffusions into Gallium Arsenide," J. Electrochem. Soc. **113**, 564–567 (1966).

[29] Boltaks, B. I., and Dzhafarov, T. D., "The Effect of Applied Electric Field on Diffusion of Impurities in Gallium Arsenide," Phys. Status Solidi **19**, 705–714 (1967).

[30] Mettler, K., "The Role of Dislocations in the Diffusion of Copper in Thermally Converted Gallium Arsenide," Solid-State Electron. **12**, 519–526 (1969).

[31] Whelan, J. M., and Fuller, C. S., "Precipitation of Copper in Gallium Arsenide," J. Appl. Phys. **31**, 1507–1508 (1960).

[32] Furukawa, Y., "Solubility and Ionization Energy of Cu, and Hole Mobility in Cu Diffused GaAs," J. Phys. Chem. Solids **26**, 1869–1877 (1965).

[33] Vasil'ev, V. S., and Kanevskii, I. N., "Determination of the Diffusion Coefficient of Impurities in Piezoelectric Semiconducting Materials," (in Russian) Fiz. Tekh. Poluprovodn. **2**, 377–381 (1968) [Sov. Phys.-Semicond. **2**, 312–315 (1968)].

[34] Vasil'ev, V. S., Kanevskii, I. N., and Osvenskii, V. G., "Measurement of the Diffusion Coefficient of Copper in Gallium Arsenide by an Ultrasonic Method," (in Russian) Fiz. Tekh. Poluprovodn. **2**, 1795–1799 (1968) [Sov. Phys.-Semicond. **2**, 1495–1498 (1969)].

[35] Hwang, C. J., "Photoluminescence Study of Defect Formation During Copper Diffusion in Zn-Doped GaAs," J. Appl. Phys. **39**, 4313–4318 (1968).

[36] Olson, F. C. W., and Schultz, O. T., "Temperatures in Solids During Heating or Cooling; Tables for the

Numerical Solution of the Heating Equation," Ind. Eng. Chem. **34**, 874–877 (1942).

[37] Kendall, D. L., *Diffusion in III–V Compounds with Particular Reference to Self-Diffusion in Indium Antimonide*, Ph.D. Thesis, Stanford Univ. (1965) 158 pp.

[38] Molchanova, S. A., "Determination of the Diffusion Coefficient of Copper and Gold in Gallium Arsenide from the Quantity of Impurity Passing into the Electrolyte in the Anode Process," (in Russian) Zh. Fiz. Khim., **46**, 2373–2374 (1972) [Russ. J. Phys. Chem. **46**, 1353–1354 (1972)].

[39] Kendall, D. L., "Simultaneous Indium and Cadmium Diffusion in Gallium Arsenide," Appl. Phys. Lett. **4**, 67–68 (1964).

[40] Frank, F. C., and Turnbull, D., "Mechanism of Diffusion of Copper in Germanium," Phys. Rev. **104**, 617–618 (1956).

[41] Fuller, C. S., and Wolfstirn, K. B., "Electrical and Transport Properties of Cu in InAs," J. Electrochem. Soc. **114**, 856–861 (1967).

[42] Boltaks, B. I., Rembeza, S. I., and Bakhadyrkhanov, M. K., "Diffusion, Solubility, and Influence of Copper on the Electrical Properties of Indium Arsenide," (in Russian) Fiz. Tverd. Tela **10**, 550–556 (1968) [Sov. Phys.-Solid State **10**, 432–437 (1968)].

[43] Fuller, C. S., and Ditzenberger, J. A., "Diffusion of Donor and Acceptor Elements in Silicon," J. Appl. Phys. **27**, 544–553 (1956).

[44] Reiss, H., Fuller, C. S., and Morin, F. J., "Chemical Interactions Among Defects in Germanium and Silicon," Bell Syst. Tech. J. **35**, 535–636 (1956).

[45] Helfmeier, H., and Feller-Kniepmeier, M., "The Effect of Impurities on the Diffusion of Copper in Nickel Single Crystals," Chapter 4.2 in *Diffusion Processes*, Vol. 1, edited by J. N. Sherwood, A. V. Chadwick, W. M. Muir, and F. L. Swinton (Gordon and Breach, New York, 1971) pp. 317–324.

[46] Helfmeier, H., *The Effect of Impurity Atoms on the Diffusion of Copper in Nickel Single Crystals* (in German), Ph. D. Thesis, Technischen Univ. Berlin (1969) 78 pp.; "The Influence of Solute Atoms on the Diffusion of Copper in Nickel Single Crystals" (in German), Z. Metallkd. **65**, 238–241 (1974).

[47] Freeman, L. A., Shaw, R. F., and Yoffe, A. D., "An Electron Microscope Study of the Diffusion of Metals in Amorphous Arsenic Triselenide Films," Thin Solid Films **3**, 367–376 (1969).

[48] Accary, A., *Study of Diffusion in Alpha Brass by Means of Evaporation and Condensation of Zinc. Influence of Diffusion Direction and the Pressure of Impurities*, (in French) Ph.D. Thesis, Univ. Paris (1957) 42 pp. (also available as CEA Rpt. No. 759) [translation available from NTC as TT 70–57557].

[49] Accary, A., "Investigation of the Diffusion in α-Brasses Using Methods Depending on the Evaporation or Condensation of Zinc," (in French) in *Colloque Sur La Diffusion A L'Etat Solide* (Proceedings of the Conference on Solid State Diffusion, Saclay, July 1958) (North Holland Publishing Co., Amsterdam, 1959) pp. 45–55 [(also available as Comm. Energ. At. (Fr.) Rapp. No. 1292, 1959) 11 pp.] [translation available from NTC as TT 71–55282].

[50] Accary, A., "Micrographic Study of the Influence of Impurities on Diffusion in Alpha Brass," (in French) C. R. Acad. Sci. **249**, 1763–1765 (1955).

[51] Accary, A., "The influence of Impurities on the Rate of Diffusion in α-Brass," (in French) C. R. Acad. Sci. **241**, 1301–1304 (1955) [translation available from NTC as TT 71–21377].

[52] Aksenov, V. V., and Kharakhorin, F. F., "Investigation of the Impurities in Glassy and Crystalline Samples of $CdGeAs_2$," (in Russian) Fiz. Tekh. Poluprovodn. **7**, 1841–1844 (1973) [Sov. Phys.-Semicond. **7**, 1231–1232 (1974)].

[53] Kharakhorin, F. F., and Aksenov, V. V., "Diffusion of Impurities in Glassy $CdGeAs_2$ at Temperatures Close to the Onset of Crystallization," (in Russian) Fiz. Tekh. Poluprovodn. **7**, 1844–1846 (1973) [Sov. Phys.-Semicond. **7**, 1233–1234 (1974)].

[54] Fisher, J. C., "Calculation of Diffusion Penetration Curves for Surface and Grain Boundary Diffusion," J. Appl. Phys. **22**, 74–77 (1951)].

[55] Sugiyama, K., "Recombination and Trapping Process at Deep Centers in N-Type GaAs," Jap. J. Appl. Phys. **6**, 601–611 (1967).

[56] Alferov, Zh. I., Garbuzov, D. Z., and Morozov, E. P., "Effect of Thermal Annealing on the Photoluminescence of Gallium Arsenide," (in Russian) Fiz. Tverd, Tela **8**, 3236–3240 (1966) [Sov. Phys.-Solid State **8**, 2589–2592 (1967)].

[57] Queisser, H. J., and Fuller, C. S., "Photoluminescence of Cu-Doped Gallium Arsenide," J. Appl. Phys. **37**, 4895–4899 (1966).

3. Copper-Bismuth

3.1. Bi*→Cu

The volume diffusion of copper into bismuth and bismuth into copper has been little studied (probably in part due to the disparity in melting points and the low solubility of copper and bismuth in each other).

Radwan and Lutze-Birk [1] were able to separate the volume and grain-boundary differential contributions in experiments where ^{210}Bi was diffused into copper in the temperature range 250–750 °C. The experiments relied on a novel technique of concentration analysis. The method is based on the measurement of x-rays formed in the β-X conversion process (in the high-energy portion of the bremsstrahlung radiation spectrum).

3.2. Cu→Cu-Bi

The reader is referred to section 3.6 for a discussion of the effect of bismuth vapors on surface self-diffusion of copper.

3.3. Cu-Bi-Te

The anisotropic diffusion of copper into the semiconductor bismuth-telluride (Bi_2Te_3) has been the object of several studies [2–4]. Stoichiometric bismuth-telluride is *p*-type, and a number of elements have been tried in order to convert it to an *n*-type semiconductor. Copper has proved to be a suitable donor impurity, but has been found (even at room temperatures) to diffuse to the surface of bismuth telluride, thus causing the material to become less *n*-type.

A marked anisotropy has been observed in the diffusion of ^{64}Cu in Bi_2Te_3 crystals [4]. This has been attributed in part to its structure. Bismuth telluride belongs to the D^5_{3d} ($R\bar{3}m$) space group with the basic unit cell being rhombohedral. In the hexagonal coordinate system, the rhombohedral [111] direction is referred to as the *c*-axis. In tables 4 and 5 the diffusion temperatures, annealing times, and computed diffusion coefficients for diffusion perpendicular and parallel to the *c*-axis are listed. The diffusion coefficients calculated for both directions of penetration as a function of reciprocal temperature are plotted in figure 14.

The diffusion of copper into bismuth telluride perpendicular to the *c*-axis can be expressed as:

$$D_{\perp}^{*}=D_0 \exp(-E/kT)=0.0034 \exp(-0.21\ \text{eV}/kT)\ \text{cm}^2/\text{s},$$

and parallel to the *c*-axis as:

$$D_{\parallel}^{*}=0.071 \exp(-0.80\ \text{eV}/kT)\ \text{cm}^2/\text{s}.$$

In view of the limited amount of data at low temperatures, and the possibility of "pipe" diffusion taking place along dislocations (which themselves have an anisotropic distribution in Bi_2Te_3), additional room-temperature investigations were undertaken [3].

TABLE 4. Tracer diffusion coefficients of ^{64}Cu in Bi_2Te_3 perpendicular to c-axis. Data of Carlson [4].

T (°C)	D* (cm²/s)
[a]450	$\approx 1.1 \times 10^{-4}$
	$\approx 8 \times 10^{-5}$
300	4×10^{-5}
285	$\approx 5 \times 10^{-5}$
200	2.0×10^{-5}
100	$\approx 7 \times 10^{-6}$
25	$\approx 6 \times 10^{-7}$
	9.0×10^{-7}
	$\approx 9 \times 10^{-7}$

[a] Measured along cleavage surface.

TABLE 5. Tracer diffusion coefficients of ^{64}Cu in Bi_2Te_3 parallel to c-axis. Data of Carlson [4].

T (°C)	D* (cm²/s)
500	8.9×10^{-7}
450	$\approx 1.0 \times 10^{-7}$
	1.8×10^{-7}
	1.8×10^{-7}
400	6.0×10^{-8}
330	1.3×10^{-8}
300	5.2×10^{-9}
263	2.8×10^{-9}
250	1.6×10^{-9}
200	$\approx 2 \times 10^{-10}$

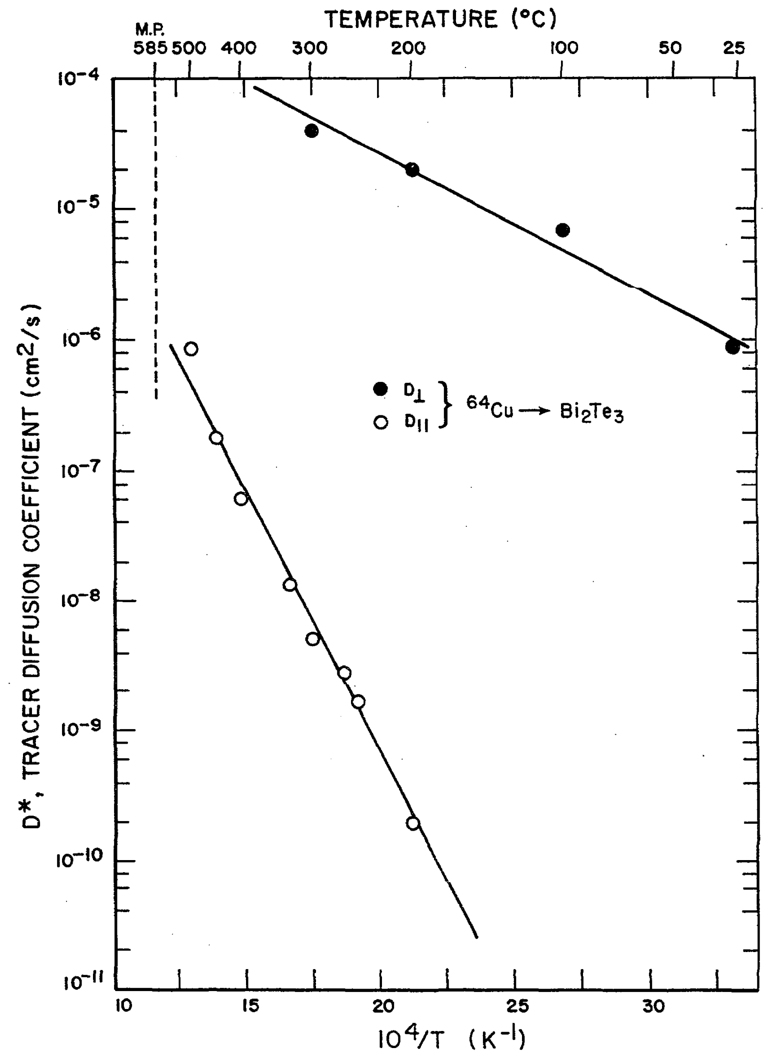

FIGURE 14. Tracer diffusion coefficients of ^{64}Cu in Bi_2Te_3 as a function of reciprocal absolute temperature.

Measurements were made both parallel and perpendicular to the c-axis, with the resulting anisotropy being readily apparent. Data from Carlson [4].

An etching technique was used to reveal copper particles (etch pits) along dislocations in Bi_2Te_3 in which copper was diffused for a few hours at room temperature. After a few days, no etch pits were observed along the dislocations. It is suggested that the etch pits observed after short diffusion times represent copper diffusion along the dislocations. It must be remembered, though, that experiments using an etching technique yield only qualitative results. No precise estimates can be made regarding the relative importance of lattice diffusion versus "pipe" diffusion at room temperatures.

For the case of diffusion perpendicular to the *c*-axis, the large diffusion coefficients would suggest interstitial diffusion. It has been rationalized [4] that for the fast diffusion in this direction, between the adjacent tellurium layers, copper moves through a region of relatively weak electrostatic bonding forces and large layer spacing. For the case of diffusion in a direction parallel to the *c*-axis, or in any other direction, the covalent and ionic bonding between bismuth and tellurium atoms make copper penetration more difficult.

3.4. Cu-Bi-X

The role of diffusion processes during the homogenization of Pb-Bi-Ag-Cu alloys was explored by Kostov [5]. No quantative diffusion data were reported in this paper.

3.5. Grain-Boundary Diffusion

The low solubility of bismuth in copper and its segregation at and in the vicinity of copper grain-boundaries with resulting embrittlement is well known. Although this embrittlement and its mechanism has been well studied, see e.g. [6–27], surprisingly little has been done in the way of grain-boudary diffusion studies. In addition to the beforementioned paper of Radwan and Lutze-Birk [1], only one other very qualitative paper was noted in the literature [28]. In this paper, high-resolution autoradiography was employed to detect the presence of bismuth in the low-bismuth content alloys. No quantitative information was reported.

The heterogeneous diffusion of liquid bismuth into polycrystalline copper has also been studied [28–30]. The results display the importance of the grain-boundary angle in controlling the diffusion of bismuth in copper (the higher the degree of misfit, the higher the diffusion rate).

Applied tensile stresses were found to accelerate the grain-boundary penetration of liquid bismuth in polycrystalline copper specimens at 500 °C [31]. With increasing uniaxial tension, the depth of penetration increased, although at low stresses some decrease in the rate of penetration was observed.

3.6. Surface Diffusion

Rhead and his coworkers [32, 33] introduced bismuth vapors as a contaminant while measuring the surface self-diffusion coefficients of copper at 900 °C. The adsorbed bismuth increased the surface self-diffusion tremendously (now referred to as "catalyzed surface-diffusion") with rates approaching the order of 1 cm^2/s. These "giant" diffusivities perhaps result from the formation of a quasi-two-dimensional, liquid surface compound, or possibly the bismuth adsorbate reacts with the copper substrate to form a surface compound (or a surface alloy) in which the copper substrate atoms are less strongly bound than in a clean surface. For further discussions of these results, see references 33–36; and for a thorough review of this topic and of other possible impurity effects, see references 37 and 38.

3.7. Electromigration

The electromigration of copper in single-crystal bismuth-telluride has been measured perpendicular to the c-axis as a function of temperature for two current-densities [2]. At a current density of 150 A/cm^2, copper transport was always in the direction of the cathode. At a current density of 250 A/cm^2, the motion of the copper was towards the cathode up to approximately 300 °C. Between 300 and 400 °C, the copper motion was bipolar. Above 400 °C, nearly all the motion was to the anode. There was an anomalous accumulation of copper within the cathode region and depletion of copper within the anode region.

The bipolar motion of the copper and the concentration anomalies within the anode and cathode regions may be the result of the layered crystal structure of bismuth telluride.

3.8. Molten Metals

The reader is referred to section 3.5 for a discussion of liquid-bismuth/solid-copper interactions.

3.9. Cu-Bi References

[1] Radwan, M., and Lutze-Birk, A., "Application of β-Radiation Excitation of X-Rays for the Investigation of Diffusion in Solids," (in German) Int. J. Appl. Radiat. Isot. **22**, 561–565 (1971).

[2] Dibbs, H. P., and Keys, J. D., "Electrotransport in Single-Crystal Bismuth Telluride," Can. J. Phys. **45**, 3945–3957 (1967).

[3] Sagar, A., and Faust, J. W., Jr., "Investigation of Copper Diffusion in Bi_2Te_3 by Etching Technique," J. Appl. Phys. **38**, 3479–3483 (1967).

[4] Carlson, R. O., "Anisotropic Diffusion of Copper into Bismuth Telluride," J. Phys. Chem. Solids **13**, 65–70 (1960).

[5] Kostov, G., "Homogenization of a Lead-Bismuth-Silver-Copper Alloy," (in Bulgarian) Rudodobiv Metal. **27**, 38–39 (1972) [translation available from NTC as TT 74–58024].

[6] Spencer, C. W., Rummel, R. A., and Rhines, F. N., "Bismuth in Copper Grain Boundaries," Trans. Metall. Soc. AIME (Am. Inst. Min. Metall. Pet. Eng.) **209**, 793–794 (1957).

[7] Voce, E., and Hallowes, A. P. C., "The Mechanism of the Embrittlement of Deoxidized Copper by Bismuth," J. Inst. Met. **73**, 323–376 (1947).

[8] McLean, D., Comment on "The Mechanism of the Embrittlement of Deoxidized Copper by Bismuth," by Voce, E. and Hallowes, A. P. C., J. Inst. Met. **73**, 791–793 (1947).

[9] Ke, T. S., "Grain Boundary Relaxation and the Mechanism of Embrittlement of Copper by Bismuth," J. Appl. Phys. **20**, 1226–1231 (1949).

[10] Samules, L. E., "The Metallography of Copper Containing Small Amounts of Bismuth," J. Inst. Met. **76**, 91–102 (1949).

[11] Cahn, R. W., "Grain Boundaries, Substructures and Impurities," in *Impurities and Imperfections* (Proceedings of the Thirty-sixth National Metal Congress and Exposition, Chicago, Ill., Oct. 30–Nov. 5, 1955) (American Society for Metals, Cleveland, 1955) pp. 41–83.

[12] Smith, C. S., "Grains, Phases, and Interfaces: An Interpretation of Microstructure," Trans. Am. Inst. Min. Metall. Eng. **175**, 15–51 (1948).

[13] Archbutt, S. L., and Prytherch, W. E., *Effect of Impurities in Copper*, Research Monograph No. 4 of the British Non-Ferrous Metals Research Assoc. (R. Clay & Sons, Limited, Bungay, Suffolk, England, 1937) pp. 56–58.

[14] Eborall, R., "Some Observations on the Mode of Occurrence of Selenium, Tellurium, and Bismuth in Copper," J. Inst. Met. **70**, 435–446 (1944).

[15] Cook, M., and Parker, G., "The Effect of Selenium, Tellurium, and Bismuth on Deoxidized Copper for Tube Manufacture," J. Inst. Met. **68**, 369–382 (1942).

[16] Bailey, G. L., and Hallowes, A. P. C., "The Properties of Commercial Coppers Containing Selenium, Tellurium, and Bismuth," J. Inst. Met. **68**, 347–368 (1942).

[17] Blazey, C., "The Influence of Various Elements on the Mechanical Properties of Copper Containing a Small Percentage of Bismuth," Proc. Australas. Inst. Min. Metall. **125**, 85–99 (1942).

[18] Blazey, C., "Brittleness in Copper," J. Inst. Met. **46**, 353–382 (1931).

[19] Blazey, C., "Brittleness in Arsenical Copper. II," J. Inst. Met. **41**, 321–328 (1929).

[20] Smith, C. S., Comment on "Brittleness in Arsenical Copper. II," by Blazey, C., J., Inst. Met. **41**, p. 328 (1929).

[21] Blazey, C., "Brittleness in Arsenical Copper," J. Inst. Met. **37**, 51–67 (1929).

[22] Johnson, F., "The Influence of Impurities in 'Tough Pitch' Copper," J. Inst. Met. **8**, 192–221 (1912).

[23] Hampe, W., "Contributions to the Metallurgy of Copper," (in German) Z. Berg-Huetten Salinenwes. Preuss. Staate **22**, 93–138 (1874).

[24] Bannister, C. O., and Doyle, W. M., "Bismuth in Copper: Its Effects, Determinations, and Some Experiments in its Gaseous Elimination," Trans. Inst. Min. Metall. **44**, 163–226 (1935).

[25] Powell, B. D., and Mykura, H., "The Segregation of Bismuth to Grain Boundaries in Copper-Bismuth Alloys," Acta Metall. **21**, 1151–1156 (1973).

[26] Stein, D. F., and Joshi, A., "Grain-Boundary Structure and Segregation," Met. Sci, J., **6**, 67–68 (1972).

[27] Joshi, A., and Stein D. F., "An Auger Spectroscopic Analysis of Bismuth Segregated to Grain Boundaries in Copper," J. Inst. Met. **99**, 178–181 (1971).

[28] Yukawa, S., and Sinott, M. J., "Diffusion of Bismuth in Copper Grain Boundaries," Trans. Metall. Soc. AIME (Am. Inst. Min. Metall. Pet. Eng.) **215**, 338–340 (1959).

[29] Scheil, E., and Schessl, K. E., "The Grain Boundary Diffusion of Bi in Cu," (in German) Z. Naturforsch. **4**, 524–526 (1949) [translation available from NTC as TT 71-55178].

[30] Feller-Kniepmeier, M., and Pawlek, F., "The Penetration of Bi into Grain Boundaries of Cu," (in German) Metall. **20**, 1156–1158 (1966) [translation available from NTC as TT 71-55279].

[31] Chaevskii, M. I., Toropovskaya, I. M., Popovich, V. V., and Datsishin, A. M., "Role of Stresses in Accelerating the Penetration of Liquid Into Solid Metals," (in Russian) Fiz. Khim. Mekh. Mater. **5**, 692–698 (1969) [Sov. Mater. Sci. **5**, 580–585 (1970)].

[32] Henrion, J., and Rhead, G. E., "On High Surface Diffusivities on Solid Metals in the Presence of Absorbed Metallic Vapours," Chapter 4.7 in *Diffusion Processes*, Vol. 1, edited by J. N. Sherwood, A. V. Chadwick, W. M. Muir, and F. L. Swinton (Gordon and Breach, New York, 1971) pp. 381–395.

[33] Biberian, J. P., and Rhead, G. E., "Surface-Self-Diffusion of Gold in the Presence of Bismuth Vapour," (in French) C. R. Acad. Sci. (Paris) **C280**, 489–492 (1975).

[34] Rhead, G. E., "On Surface Diffusion and the Existence of 'Two-Dimensional' Liquids," Surf. Sci. **15**, 353–357 (1969).

[35] Bonzel, H. P., and Gjostein, N. A., Comment on "Surface Diffusion and the Existence of 'Two-Dimensional' Liquids," by Rhead, G., Surf. Sci. **22**, 216–222 (1970).

[36] Rhead, G. E., Reply to Comment on "Surface Diffusion and the Existence of 'Two-Dimensional' Liquids," Surf. Sci. **22**, 223–228 (1970).

[37] Rhead, G. E., "Diffusion on Surfaces," Surf. Sci. **47**, 207–221 (1975).

[38] Bonzel, H. P., "Surface Diffusion of Metals," in *Structure and Properties of Metal Surfaces*, eidted by S. Shimodaira (Maruzin, Japan, 1972).

4. Copper-Nitrogen

4.1. N→Cu

No diffusion coefficients have been measured for nitrogen in pure copper. Diffusion studies have probably been inhibited by knowledge of the insolubility of nitrogen in solid or liquid copper [1–4], or even chemisorb on copper [5, 6]. Absorption of nitrogen, if it exists at all, is believed to be minimal [7–9]. Those few early references [10–14] on measurements in solid copper record no penetration rates. Reaction of nitrogen gas with solid copper has been reported as occurring above 900 °C [15]. The formation of a nitride, Cu_3N, has also been recorded [15–22], although ammonia gas (NH_3) was employed rather than pure nitrogen.

4.2. Cu-N References

[1] Sieverts, A., and Krumbhaar, W., "On the Transport of Gases in Metals and Alloys," (in German) Ber. Dtsch. Chem. Ges. **43**, 893–900 (1910).

[2] Sieverts, A., and Krumbhaar, W. (in German) Z. Phys. Chem. Stoechiom. Verwandschaftsl. **74**, 277–307 (1910).

[3] Lobley, A. G., and Jepson, D., "The Influence of Gases on Copper at High Temperatures. Part I." J. Inst. Met. **35**, 213–229 (1926).

[4] Rontgen, P., and Moller, F. (in German) Metallwirtsch. **13**, 31–83, 97–100 (1934).

[5] Taylor, H. S., J. Ind. Eng. Chem. **13**, p. 75 (1921).

[6] Trapnell, B. M. W., Proc. R. Soc. Edinburgh, Section A, **218**, p. 566 (1953).

[7] Pope, L. E., and Olson, F. A., "Degassing of Copper Wires in an Ultrahigh Vacuum: Part I. Diffusion," Metall. Trans. **2**, 2711–2716 (1971).

[8] Basalaeva, N. Ia., "Evolution of Gas in Metals used in Vacuum Technology," (in Russian) Zh. Tekh. Fiz. **28**, 1102–1107 (1958) [Sov. Phys.-Tech. Phys. **3**, 1027–1031 (1958)].

[9] Ryder, H. M., "The Quantitative Analysis of Small Quantities of Gases," J. Am. Chem. Soc. **40**, 1656–1662 (1918).

[10] DeBoer, J. H., and Fast, J. D., "Diffusion of Water Vapor through Copper," (in German) Recl. Trav. Chim. Pays-Bas, **54**, 970–974 (1935) [translation available from NTC as TT 71-55166].

[11] Anonymous, "The Diffusion of Gases through Metals," Metallurgist (London) **6**, 24–25 (1930).

[12] Anonymous, "The Diffusion of Gases through Metals," Metallurgist (London) **10**, 68–71 (1935–1936).

[13] Anonymous, "The Diffusion of Gases through Metals," Metallurgist (London) **10**, 113–115 (1935–1936).

[14] Smithells, C. J., and Ransley, C. E., "The Diffusion of Gases through Metals," Proc. R. Soc. Lond. **A150**, 172–196 (1935).

[15] Laffitte, P., and Grandadam, P., "Organic Chemistry on the Nitriding of Several Metals," (in French) C. R. Acad. Sci. **200**, 1039–1041 (1935) [translation available from NTC as TT 71-55225].

[16] Matignon, C., and Trannov, R., "General Catalytic Oxidation in a Lamp Flame," (in French) C. R. Acad. Sci. **142**, 1210–1211 (1906).

[17] Juza, R., "An Observation of the Crystal Structure of Cu_3N," (in German) Z. Anorg. Allg. Chem. **248**, 118–120 (1941).

[18] Guntz, MM. A., and Bassett, H., "The Nitriding of Copper," (in French) Bull. Soc. Chim. **3**, 201–207 (1906).

[19] Juda, R., and Hahn, H., "On the Crystal Structure of Cu_3N, GaN, and InN," (in German) Z. Anorg. Allg. Chem. **239**, 282–287 (1938).

[20] Juda, R., and Hahn, H., "Copper Nitride," (in German) Z. Anorg. Allg. Chem. **241**, 172–178 (1939).

[21] Schrotter, A. (in German), Liebigs. Ann. Chem. **37**, p. 131 (1841).

[22] Warren, H.N., Chem. News **55**, p. 156 (1887).

5. Copper-Phosphorus

Diffusion in the copper-phosphorus binary has been little studied. Except for a few semi-qualitative interdiffusion studies [1–3], no other papers could be located.

5.1. Cu-P Interdiffusion

In one of the above-mentioned investigations [1, 2], pure copper was interdiffused with phosphorus vapor at temperatures ranging from 350 to 450°. The principal goal in the experiment was the following of the diffusion growth of the compound Cu_3P, rather than the measurement of any diffusion coefficients. In the other study, copper is packed in powdered Cu_3P and interdiffused in the temperature range 400–800 °C for as long as 200 hours to produce an alloy of the two constituents.

5.2. Cu-P-Fe

Sirca [4–6] interdiffused copper, containing small amounts of phosphorus (up to 1.2%) and iron at temperatures up to 1100 °C. His results indicate that the phosphorus additions minimized the amount of copper diffusion down the iron grain-boundaries.

The changes in the microstructure of Fe-Cu alloys induced by the diffusion of phosphorus (from a vapor phase) at 1950 °C were observed by Claussen [7]. The results were much the same as those observed in low-carbon steels. Hauk [8] concludes in her review that phosphorus accelerates copper mobility in steel.

5.3. Cu-P-In

The tracer-impurity diffusion coefficient of ^{64}Cu in the semiconducting compound InP has been determined in the temperature range 600–900 °C [9].

Radioactive ^{64}Cu was either electrolytically or chemically deposited on the surfaces of *n*-type InP (electron concentration $n=2.2$ to 3.8×10^{17} cm^3 and mobility $\mu m=3{,}700$ cm^2/V·s at 300 K) that was presumably single crystalline. The pre-diffusion anneals, as well as the diffusion annealing procedures, are described in detail elsewhere [10–13]. The concentration distribution of ^{64}Cu in InP was arrived at via the technique of Boltaks [14] and, as with the diffusion of copper-impurity in other semiconducting compounds of the A^{III} B^{V} type, the usual distribution described by the *erfc* function was not obtained. The complicated nature of a typical concentration curve for ^{64}Cu in InP is illustrated in figure 15. The copper concentration distribution deep in the body of the specimen can be described by the function, *erfc* $[X/2(Dt)^{1/2}]$, and an effective impurity diffusion coefficient determined. These values are plotted as a function of reciprocal temperature in figure 16. The temperature dependence of this diffusion coefficient can be expressed by the following equation:

$$D_{\mathrm{effective}}=3.8\times10^{-3}\exp(-0.69\pm0.02\ \mathrm{eV}/kt)\ \mathrm{cm}^2/\mathrm{s}.$$

The rapid migration of copper in InP certainly contains a great deal of interstitial character—the operating mechanisms yet to be exactly determined.

5.4. Cu-P-Si

The phosphorus diffusion gettering of copper in silicon has been reported [15].

5.5. Cu-P-Zn

Over a period of years, Accary has published a series of papers [16–20] describing his experiments on the role of trace amounts of phosphorus impurities on the diffusion processes in α-brasses.

In a 70/30 alloy of Cu-Zn, the addition of 0.005 to 0.1 at.% phosphorus resulted in increased weight losses (zinc evaporation) and porosity in specimens annealed at 780 °C [17–20]. The data obtained from these evaporation (and condensation) experiments

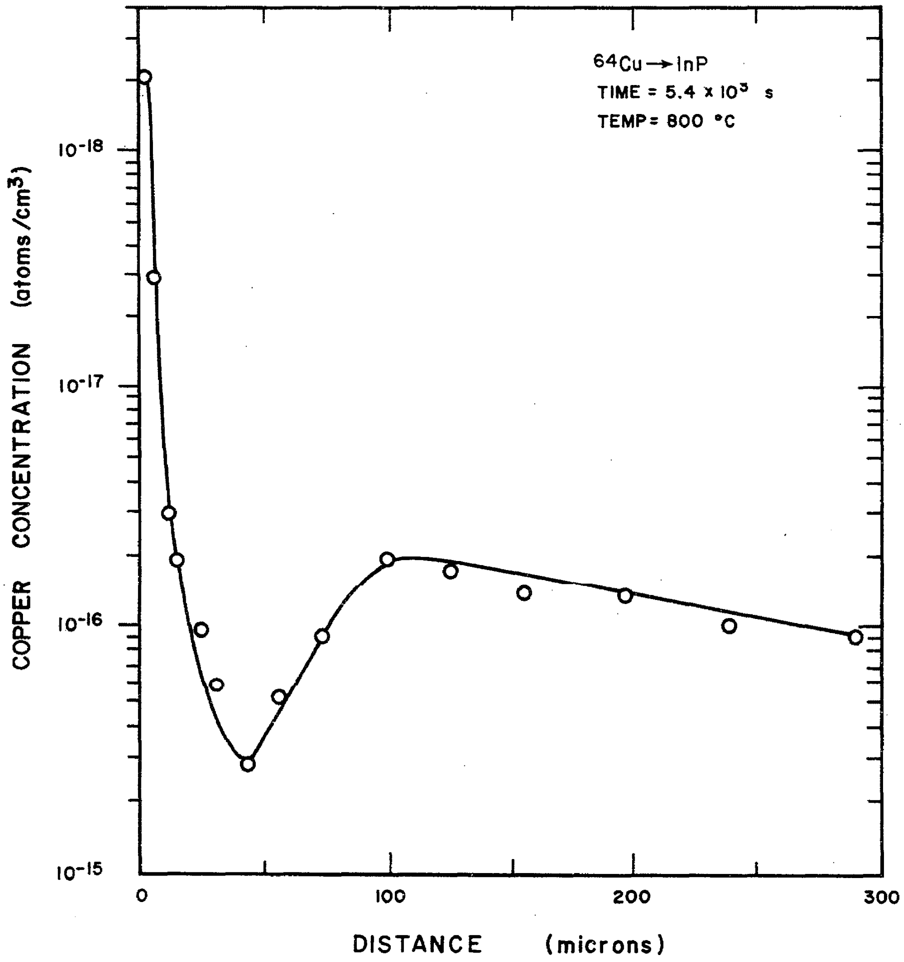

FIGURE 15. Concentration distribution of ^{64}Cu in n-type InP at 800 °C.

Data from Arseni [9].

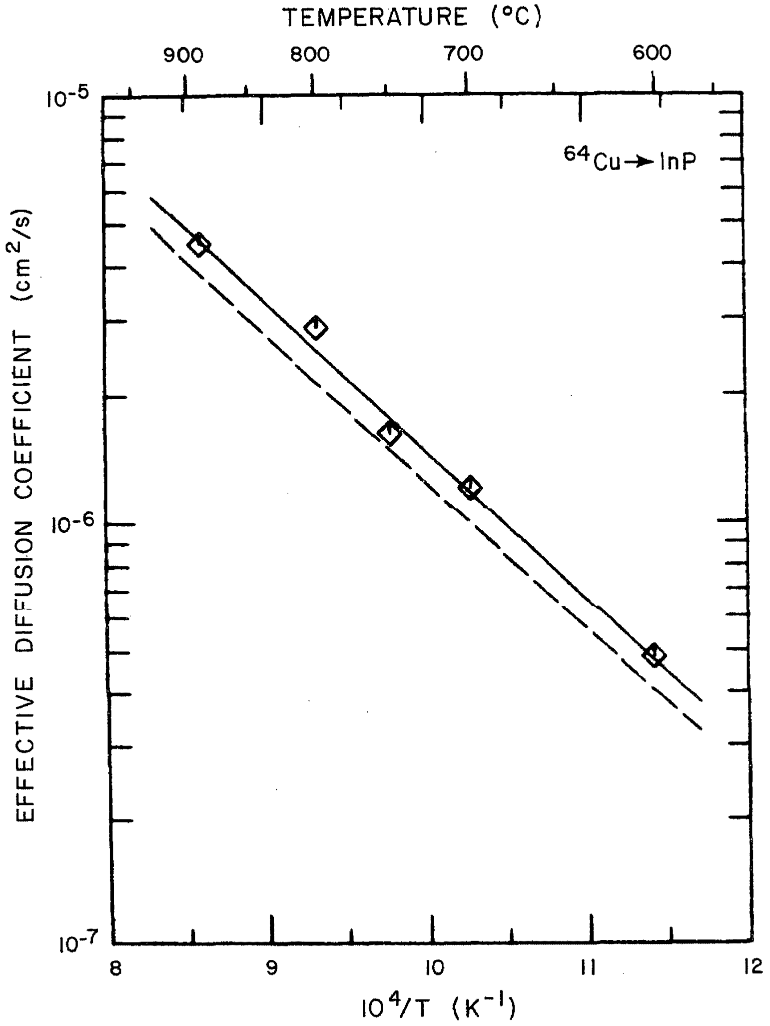

FIGURE 16. Effective diffusion coefficients of ^{64}Cu in InP as a function of reciprocal absolute temperature from the data of Arseni [9].

The dashed line is Arseni's stated line with $D_0=3.8\times10^{-3}$ cm²/s, and $Q=0.69$ eV. The solid line is a least-squares line with $D_0=4.62\times10^{-3}$ cm²/s, and $Q=0.693$ eV.

led Accary to conclude that phosphorus additions increased the self-diffusion rate of zinc in his alloys.

Interdiffusion experiments were also performed [16, 20] at 800 °C with couples constructed of copper (containing 0.015 to 1 at.% P) and brass (containing approximately 30 at.% Zn and 0.015–0.060 at.% P). Diffusion couples were also constructed of phosphorus-free alloys for comparison. In all configurations, marker motion was toward the brass side of the couple, although the size of the Kirkendall effect appeared to be quite dependent on phosphorus content in the metals used to construct the couple.

5.6. Cu-P References

[1] Arkharov, V. I., and Mardeshev, S., "The Mechanism of Reactional Diffusion in the Interaction of Solid Copper with some Gaseous Elements," (in Russian) Dokl. Akad. Nauk SSSR **103**, 273–276 (1955) [translation available from NTIS as TT 74-53072].

[2] Arkharov, V. I., and Mardeshev, S., "X-Ray Study of Reaction Diffusion in Binary Systems Composed of Copper with the Halides, with Phosphorus, and with Silicon," (in Russian) Fiz. Met. Metalloved. **1** (3) 510–516 (1955).

[3] David, F., and David, J., Inventors; "Thermal Diffusion Process for Preparing Phosphorus-Containing Copper," French Patent 2,043,883 (1969) 4pp.

[4] Zumer, M., and Sirica, F., "Some Phenomena in the Diffusion of Copper into Iron," (in Slovenian) Rud. Met. Zb. No. 1, 25–33 (1955) [translation available from NTC as TT 70-56040].

[5] Sirca, F., "Influence of Alpha Forming Elements on the Diffusion of Copper in Gama Iron," (in French) Mem. Sci. Rev. Metall. **57**, 879–887 (1960) [translation available from NTC as TT 70-57918].

[6] Sirca, F., "Influence of Alpha-forming Elements on the Diffusion of Copper into Gama Iron. Part II," (in Slovenian) Rud. Met. Zb. No. 4, 377–387 (1961) [translation available from NTC as TT 70–56048].

[7] Claussen, G. E., "The Diffusion of Elements in Solid Iron," Trans. Am. Soc. Met. **24**, 640–648 (1936).

[8] Hauk, J., "On the Influence of a Third Element in the Case of Diffusion in Metals," (in German) Metallforschung **2**, 49–56 (1947) [translation available from NTC as TT 70–58123].

[9] Arseni, K. A., "The Diffusion and Solubility of Copper in Indium Phosphide," (in Russian) Fiz. Tverd. Tela **10**, 2864–2866 (1968) [Sov. Phys.-Solid State **10**, 2263–2264 (1969)].

[10] Arseni, K. A., Boltaks, B. I., Gordin, V. L., and Ugai, Ya. A., "Diffusion and Solubility of Cadmium in Indium Phosphide," (in Russian) Izv. Akad. Nauk SSSR, Neorg. Mater. **3**, 1679–1681 (1967) [Inorg. Mater. **3**, 1465–1467 (1967)].

[11] Boltaks, B. I., Rembeza, S. I., and Sharma, B. L., "Diffusion Solubility, and Charge of Silver in Indium Arsenide," (in Russian) Fiz. Tekh. Poluprovodn. **1**, 247–264 (1967) [Sov. Phys.-Semicond. **1**, 196–201 (1967)].

[12] Arseni, K. A., Boltaks, B. I., and Rembeza, S. I., "Diffusion and Solubility of Cadmium in Indium Arsenide," (in Russian) Fiz. Tverd. Tela **8**, 2809–2811 (1966) [Sov. Phys.-Solid State **8**, 2248–2249 (1967)].

[13] Arseni, K. A., "Diffusion of Phosphorus in Indium Arsenide," (in Russian) Fiz. Tekh. Poluprovodn. **2**, 444–446 (1968) [Sov. Phys.-Semicond. **2**, 367–368 (1968)].

[14] Boltaks, B. I., Dzhafarov, T. D., Sokolov, V. I., and Shishiyanu, F. S., "Diffusion and Electrical Transport of Zinc in Gallium Arsenide," (in Russian) Fiz. Tverd. Tela **6**, 1511–1519 (1964) [Sov. Phys.-Solid State **6**, 1181–1188 (1964)].

[15] Seidel, T. E., and Meek, R. L., "Ion Implantation Damage Gettering and Phosphorus Diffusion Gettering of Copper and Gold in Silicon," in *Ion Implantation Semicond. Other Mater.* (Proceedings of the 3rd International Conference, 1972) edited by B. L. Crowder (Plenum Press, New York, 1973) pp. 305–315.

[16] Accary, A., "Influence of Phosphorus on Kirkendall-Smigelskas Effect in Copper-Brass Couples," (in French) C. R. Acad. Sci. **238**, 1120–1122 (1954) [translation available from NTC as TT 70–57588].

[17] Accary, A., "The Influence of Impurities on the Rate of Diffusion in α-Brass," (in French) C. R. Acad. Sci. **241**, 1301–1304 (1955) [translation available from NTC as TT 71–21377].

[18] Accary, A., "Micrographic Study of the Influence of Impurities on Diffusion in Alpha Brass," (in French) C. R. Acad. Sci. **241**, 1763–1765 (1955).

[19] Accary, A., "Investigation of the Diffusion in α-Brasses Using Methods Depending on the Evaporation or Condensation of Zinc," (in French) in *Colloque Sur La Diffusion A L'Etat Solide* (Proceedings of the Conference on Solid State Diffusion, Saclay, July 1958) (North Holland Publishing Co., Amsterdam, 1959) pp. 45–55 [also available as Comm. Energ. At. (Fr). Rapp. No. 1292 (1959), 11 pp.] [translation available from NTC as TT 71–55282].

[20] Accary, A., *Study of Diffusion in Alpha Brass by Means of Evaporation and Condensation of Zinc. Influence of Diffusion Direction and the Presence of Impurities* (in French), Ph.D. Thesis, Univ. Paris (1957) 42 pp. (also available as CEA Rpt. No. 759) [translation available from NTC as TT 70–57557].

6. Copper-Antimony

6.1. Sb*→Cu

The rate of diffusion of antimony in copper single crystals (99.99% purity) was measured over the temperature range 600–1000 °C by means of a sectioning technique employing the ^{124}Sb radioisotope as a tracer [1]. The temperature dependence of the diffusion coefficient closely followed the Arrhenius relation:

$$D^* = (0.34 \pm 0.12) \exp[-(42.0 \pm 0.7) \text{ kcal mol}^{-1}/RT] \text{ cm}^2/\text{s},$$

and the quoted errors correspond to 90% reliability limits. The results are summarized in the graph (figure 17) of D vs. $1/T$. Additionally, plots of the ln (specific activity) vs. (penetration depth)^2 and ln D vs. $1/T$ were linear, indicating the absence of any extraneous diffusion processes.

Measurements of the impurity diffusion of antimony in copper [2] (made with the assistance of an electron-microprobe analyzer) in the temperature range 700–850 °C are in good agreement with the above-mentioned tracer data [1].

A very careful autoradiographic study [3, 4] over the temperature range 560–896 °C produced results

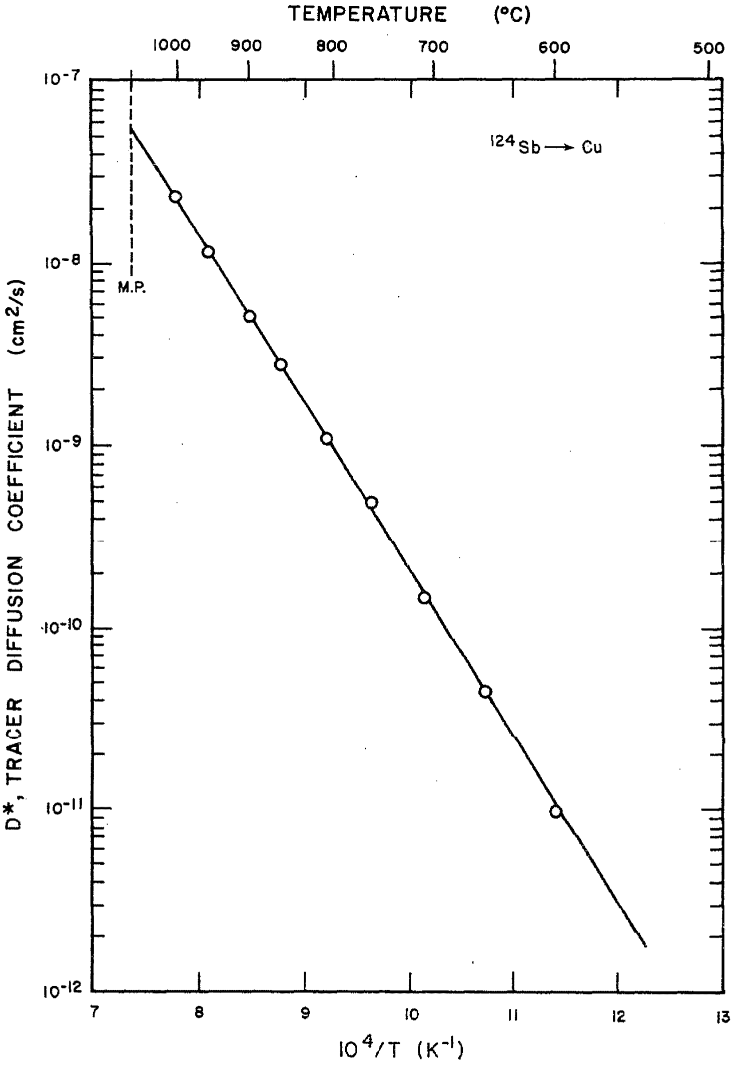

FIGURE 17. Tracer diffusion coefficients of ^{124}Sb in single-crystal copper as a function of reciprocal absolute temperature.

Data from Inman and Barr [1].

which are in good agreement with the results obtained from mechanical sectioning [1] and chemical sectioning [5]. In the autoradiographic experiments performed at low temperatures (540–630 °C) and with small penetration depths, anomalously low values of the diffusion coefficient were obtained [3, 5] when compared to the results of mechanical sectioning [1] extrapolated to these lower temperatures.

To clarify this disagreement, a technique of chemical sectioning was developed by which sections down to 1 μm thick could be removed from the surface of copper single crystals [5]. By means of this technique, diffusion coefficients for ^{124}Sb diffusing into single crystals of 99.99% copper were obtained using diffusion depths of only 10 to 15 μm and an accuracy to ±12%. Temperatures ranged between 540 and 600 °C. Although the experiments were carefully performed, only three samples were used. Three additional samples were used, but with a strain applied to see if there was any enhancement of diffusivity. No enhancement was observed, and these data (corrected for the longitudinal-strain condition) are plotted in figure 18 with those samples used without strain.

It is apparent that when one compares the results obtained from mechanical-sectioning techniques with those from chemical-sectioning experiments involving small diffusion depths, there is a considerable difference in the diffusion coefficients. Whether this difference is real or not, might be questioned because of the difficulty of performing the chemical-sectioning experiment and the few samples used. However, in view of the apparent care used in performing the experiment, this difference very likely is real, indicating a negative enhancement for diffusion near the surface. Whether this enhancement is due to a vacancy deficiency in the region of the free surface or to some other condition, is still open to question.

An early autoradiographic study [6] yielded somewhat poorer data. Using single crystals of high-purity copper (99.9987 wt%) over the temperature range 700–900 °C, the plot shown in figure 19 was obtained from the average values of the results. The diffusion coefficient was expressed as:

$$D_{\mathrm{Sb}^*\rightarrow\mathrm{Cu}}=35.5\exp[-(48.2\pm0.5)\ \mathrm{kcal{\cdot}mol^{-1}}/RT]\ \mathrm{cm^2/s}.$$

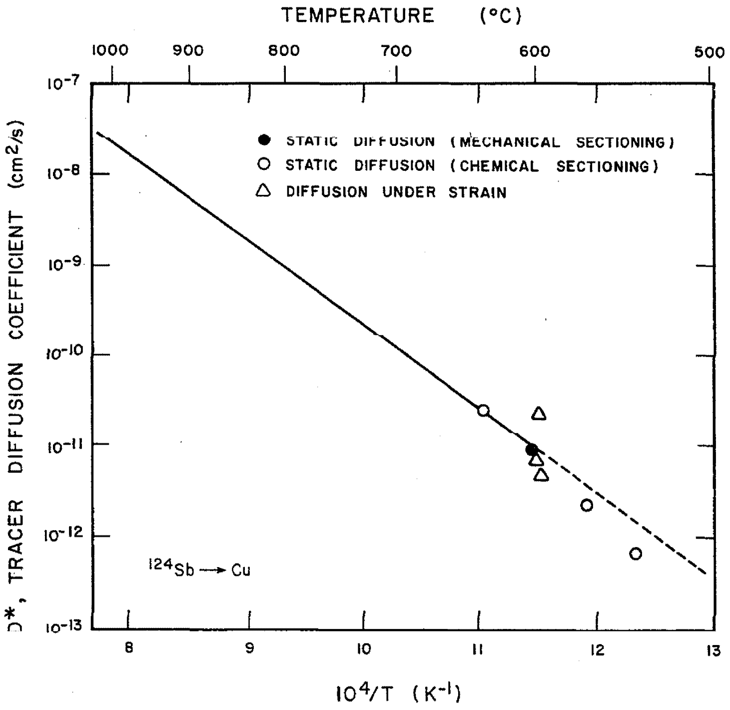

FIGURE 18. Tracer diffusion coefficients of ^{124}Sb in single-crystal copper by a chemical-sectioning technique and with the influence of strain as a function of reciprocal absolute temperature.

The solid line is the Arrhenius equation of Inman and Barr [1], with the dashed line being an extrapolation to this line. Data from Barr et al. [5].

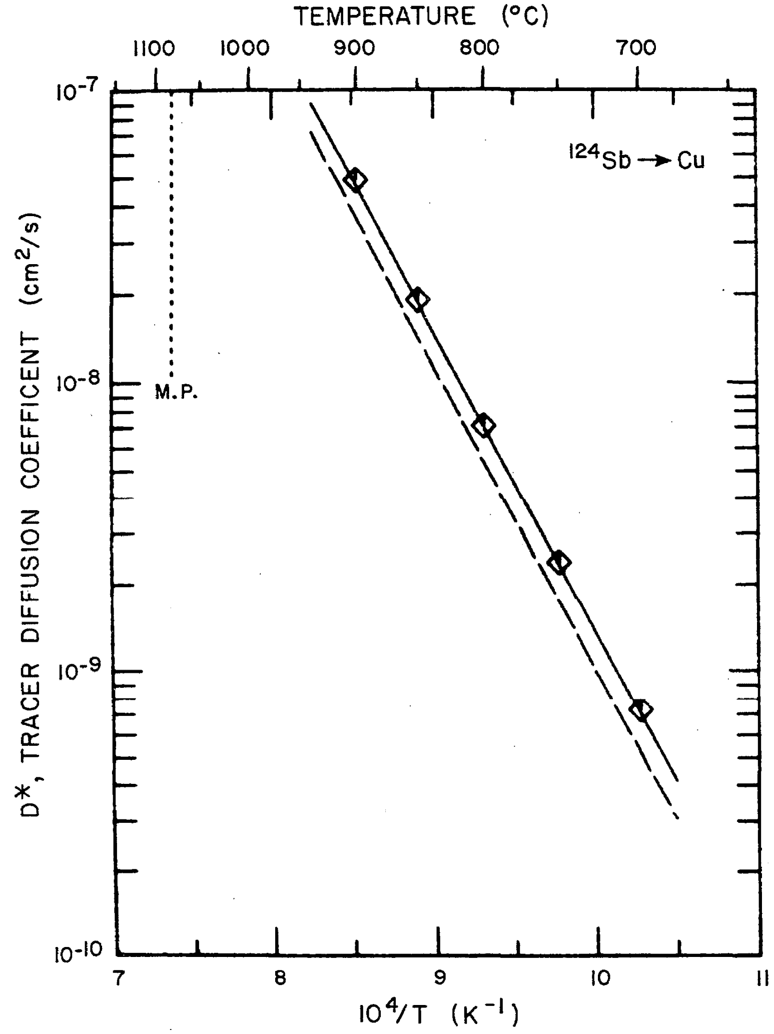

FIGURE 19. Tracer diffusion coefficients of ^{124}Sb in single-crystal copper by autoradiography as a function of reciprocal absolute temperature from the data of Gertsriken and Revo [6].

The dashed line is the authors' stated line with $D_0=35.5$ cm^2/s, and $Q=48.2$ kcal/mol. The solid line is a least-squares line with $D_0=34.77$ cm^2/s, and $Q=47.6$ kcal/mol.

The value of the pre-exponential seems to be high, as well as the value for the activation energy. This disparity in values with those obtained for other impurities diffusing in copper makes one wonder if a serious experimetal error took place.

At the single temperature of 390 °C, a determination has been made by Heumann and Heinemann [7] using a tracer-sectioning technique. They reported an average value of 2.9×10^{-13} cm^2/s for the ^{124}Sb diffusion coefficient.

Electromigration and strain-enhanced diffusion of antimony in copper are discussed later in sections 6.13 and 6.15 respectively, of this Cu-Sb system.

6.2. Cu*→Sb

Only one reference could be found for the diffusion of ^{64}Cu in pure antimony, that of the previously-mentioned study of Heumann and Heinemann [7]. The measurement was made concurrent with the other determinations in alloys at 390 °C and utilized a tracer-sectioning technique developed first by Steigman and co-workers [8]. Short diffusion times (5.2 and 8.2 hours) coupled with low annealing temtures limited the accuracy of the measurements. An average, tracer diffusion coefficient of $\approx10^{-14}$ cm^2/s was reported.

6.3. Sb*→Cu-Sb

Concurrent with their measurements in pure metals, Heumann and Heinemann made multiphase diffusion studies [7]. Radioactive ^{124}Sb was diffused into alloy specimens whose compositions varied from 31.5 to 48.6 wt% antimony (see table 6) at a temperature of 390 °C. The equilibrium diagram at these compositions and temperatures is complex, possessing a number of phases which exist over a limited composition and temperature ranges. At the time of their study (1956), the authors denoted the existence of three separate phases at that temperature and in that composition range. Tracer diffusion coefficients were measured in each of the three single-phase regions, labeled δ(31.5 wt% Sb), κ(38.2 wt% Sb), and γ(48.6 wt% Sb). Accurate measurements were made difficult by the relatively low temperatures of the diffusion anneals and resultant short penetration distances, brittleness of the intermetallic phases, polycrystalline specimens, etc. In spite of these experimental difficulties, the authors were able to arrive at values for the antimony tracer diffusion coefficients. The average values calculated from several experiments are listed in table 6, along with the results obtained in the pure metals for comparison. Although the authors report no errors, they had to be considerable.

TABLE 6. Tracer diffusion coefficients of ^{124}Sb in some phases of the Cu-Sb system at 390 °C. The values listed are the average of several experiments. The results for pure metals are also shown for comparison. Data from Heumann and Heineman [7].

Phase	Composition (wt% Sb)	D^*_{Sb} (cm^2/s)
Cu	0	2.9×10^{-13}
δ	31.5	3×10^{-11}
κ	38.2	3.1×10^{-10}
γ	48.6	2.7×10^{-9}
Sb	100	1.5×10^{-11}

6.4. Cu*→Cu-Sb

Concurrent with the measurements made with ^{124}Sb (see the previous section, Sb*→Cu-Sb), Heumann and Heinemann [7] followed the tracer diffusion of ^{64}Cu in alloys of the same composition of the Cu-Sb binary (see table 7). Because of the short half-life of the copper isotope, the experimental technique developed by Steigman, Shockley and Nix [8] was employed, and short diffusion anneals (maximum 8.2 hours) were required. This, as well as the other difficulties mentioned previously, all contributed to reduced accuracy in the final values of the coefficients. The average values (calculated from three determinations) are listed in table 7 along with data obtained from their experiments with the pure metals.

TABLE 7. Tracer diffusion coefficients of ^{64}Cu in some phases of the Cu-Sb system at 390 °C. The values listed are the average of several experiments. The results for pure metals are also shown for comparison. Data from Heumann and Heineman [7].

Phase	Composition (wt% Sb)	D^*_{Cu} (cm^2/s)
Cu	0	$\approx 10^{-14}$
δ	31.5	4×10^{-10}
κ	38.2	7×10^{-9}
γ	48.6	$\approx 10^{-9}$
Sb	100	3×10^{-10}

More recently Heumann and his co-workers [9] measured copper self-diffusion coefficients in the high-temperature β-phase (Cu_3Sb) of the Cu-Sb system. The composition range extended from 21 to 29 at.% Sb. The temperature of the study varied from 520 to 630 °C. Gruzin's sectioning technique [10] was employed. The extraordinarily high tracer diffusion coefficients they obtained are plotted in figure 20 as a function of reciprocal absolute temperature. The straight line is a least-squares fit to the data. The frequency factors and activation energies for the appropriate Arrhenius expressions describing these straight lines are given in table 8 along with the author's estimated errors.

The composition dependence of the diffusion coefficient of ^{64}Cu is illustrated in figure 21.

The authors attribute the high ^{64}Cu mobility (and composition dependence of the activation energy) to the defect structure of β-Cu_3Sb.

6.5. Cu-Sb Interdiffusion

Interdiffusion investigations in the Cu-Sb system have been largely directed at following layer-growth in the diffusion zone [7, 9, 11–16]. The earliest work,

TABLE 8. Arrhenius parameters for the tracer diffusion of ^{64}Cu in β-Cu_3Sb. Data from Heumann et al. [9].

Cu-Sb Alloy (at.% Sb)	D_0 (cm^2/s)^a	Q (kcal/mol)
21	8.57×10^{-4}	10.46 ± 1.34
25	1.99×10^{-4}	7.26 ± 1.01
29	1.36×10^{-4}	5.80 ± 0.87

[a] Pre-exponential values decreased by 10^{-1} so as to agree with the authors' plotted data in figure 20.

that of Weiss [11–13], yielded no diffusion coefficients. Subsequent study in thin films [14] gave results inconsistent with more recent investigations.

Interdiffusion experiments were performed at 593 °C within the high-temperature β-phase (Cu_3Sb) of this binary [9]. Couples were constructed of alloys containing 20.6 at.% Sb and 28.1 at.% Sb. Concentration-penetration curves were determined with the aid of an electron microprobe analyzer. Partial diffusion coefficients for copper were calculated (using Heumann's method [17]) for a concentration of 25.3 ± 0.2 at.% Sb. These are plotted in figure 22 as a function of reciprocal absolute temperature. A straight line was fitted to the data by the least-squares method, and an activation energy of 5.67 ± 0.92 kcal/mol was calculated.

In addition to their tracer experiments at 390 °C, Heumann and Heinemann [7] performed several interdiffusion experiments which allowed them to calculate a partial diffusion coefficient for copper in the β-phase (37.9–39.6 wt% Sb) of 4×10^{-7} cm^2/s. The interdiffusion coefficient in the β-phase was 1.3×10^{-7} cm^2/s, and in the γ-phase (Cu_2Sb), 6.9×10^{-8} cm^2/s.

Interdiffusion between pure copper and antimony under a compressive stress has also been examined [7, 15, 16] and is discussed later in section 6.15 dealing with stress-enhanced diffusion.

6.6. Cu-Sb-Ag

An early study of both volume and grain-boundary diffusion of silver in Cu-Sb alloys found that the silver mobility was enhanced with increasing antimony additions to the alloy [18, 19]. Polycrystalline silver wires were inserted into the core of the Cu-Sb specimens to form interdiffusion couples. The Cu-Sb alloys contained from 0.003 to 4.72 wt% antimony and were of varying grain size. The diffusion anneals took place between 630 and 700 °C, ranging in time from 69 to 101 hours. After quenching, the microstructure and width of the interdiffusion zones were examined micrometallographically. From their observations the authors concluded that the mobility of silver within the Cu-Sb alloys increased with increasing percentage of antimony, as well as with decreasing grain size. Interdiffusion zone widths were found to increase correspondingly. In those experiments utilizing high antimony contents (≈4.7 wt%), it was found that grain-boundary diffusion contributions of silver dropped off due to increased volume diffusion.

The addition of 0.25% antimony (unspecified, but quite probably wt%) to copper will speed up the rate of diffusion of radioactive silver in the alloy grain-boundaries at 650 °C when compared to pure copper [20]. The antimony alloying addition appeared to alter the orientation dependence found for pure-copper specimens [21].

6.7. Cu-Sb-Al

The interdiffusion characteristics of the ternary system Cu-Al-Sb were studied qualitatively by Kelly [22]. No interdiffusion coefficients were determined. In these experiments a Cu-Al(11.4 at.%) alloy was diffused with a Cu-Sb(0.62 at.%) alloy. After heating at 900 °C, visible "bands," normal to the direction of diffusion and parallel to the interface, were observed. A mathematical model based on the maximum rate of change in concentration of the diffusants was offered to describe the phenomena.

In the semiconductor area, radioactive ^{64}Cu has been diffused into the semiconductor compound AlSb in the temperature range 150–500 °C [23]. Although there was appreciable scatter in the data, an activation energy (0.36eV) and pre-exponential factor (3.5×10^{-3} cm^2/s) was determined. The copper tracer diffusion coefficients are plotted in figure 23 as a function of reciprocal absolute temperature. Although the activation energy for diffusion is quite low, it is typical for the diffusion of copper (and other impurities) whose diffusion properties possess semi-interstitial character.

6.8. Cu-Sb-Fe

The addition of antimony (up to 8%) to copper was found to hinder copper interdiffusion when the alloys were interdiffused with pure iron at 1000 °C [24, 25]. The decelerating effect increased with increased antimony content. There appeared to be little or no effect of the antimony on the migration of copper in the iron grain-boundaries.

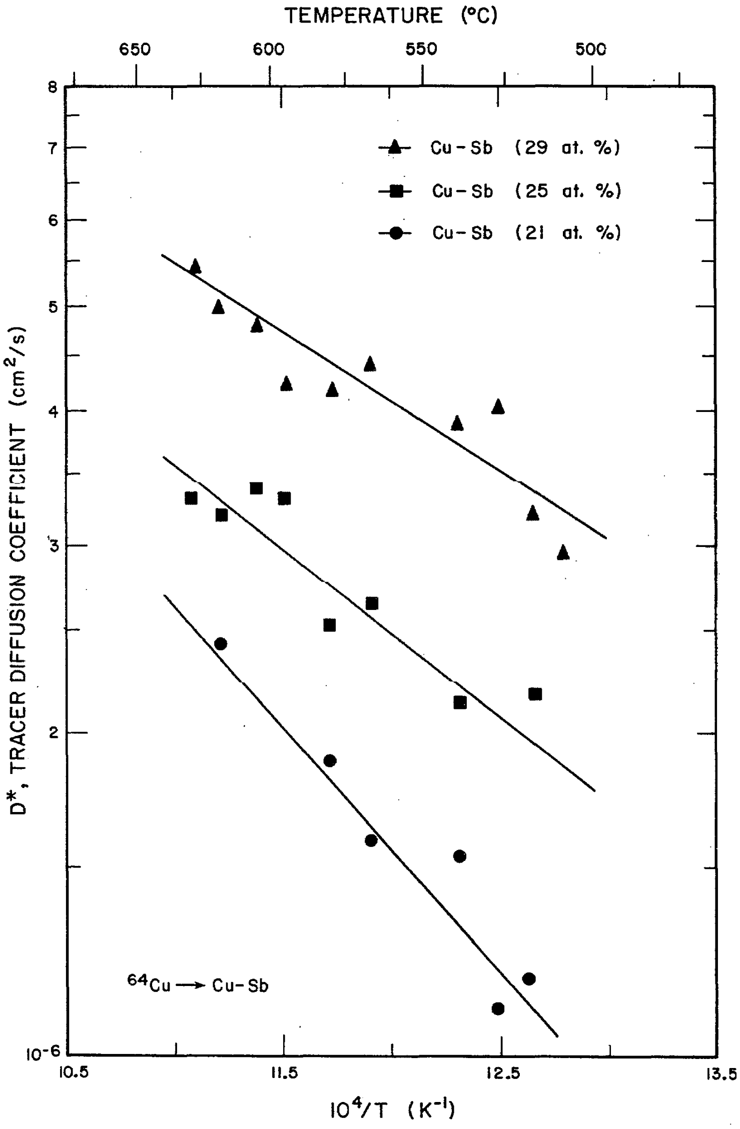

FIGURE 20. Tracer diffusion coefficients of ^{64}Cu in β-Cu_3Sb as a function of reciprocal absolute temperature.

The plotted data points are from interpolation of the authors' graphs. The lines are the authors' quoted values with a correction, as noted in table 8. Data from Heumann et al. [9].

6.9. Cu-Sb-Ga

The tracer diffusion of copper in tellurium-doped, *p*- and *n*-type GaSb has been reported for the temperature range 470–650 °C [26]. Vapor pressure of the antimony was maintained at approximately one atmosphere above the specimens during diffusion. The complex concentration profiles of the ^{64}Cu were determined by conventional sectioning of the specimens. A higher ^{64}Cu concentration was noted in the surface layers, with the bulk portion of the ^{64}Cu distribution described aptly by the *erfc* function. The author draws a straight line through his four experimental points and describes it with the following Arrhenius expression:

$$D_{Cu}^* = 4.7 \times 10^{-3} \exp(-0.90 \text{ eV}/kT) \text{ cm}^2/\text{s}.$$

No errors were specified.

Electromigration experiments [27] were performed with the same specimens in the same temperature range (450–650 °C). In the tellurium-doped and zinc-doped *n*-type crustals, ^{64}Cu migrated preferentially towards the cathode. In contrast to this behavior, ^{64}Cu migrated towards the anode in zinc-doped *p*-type

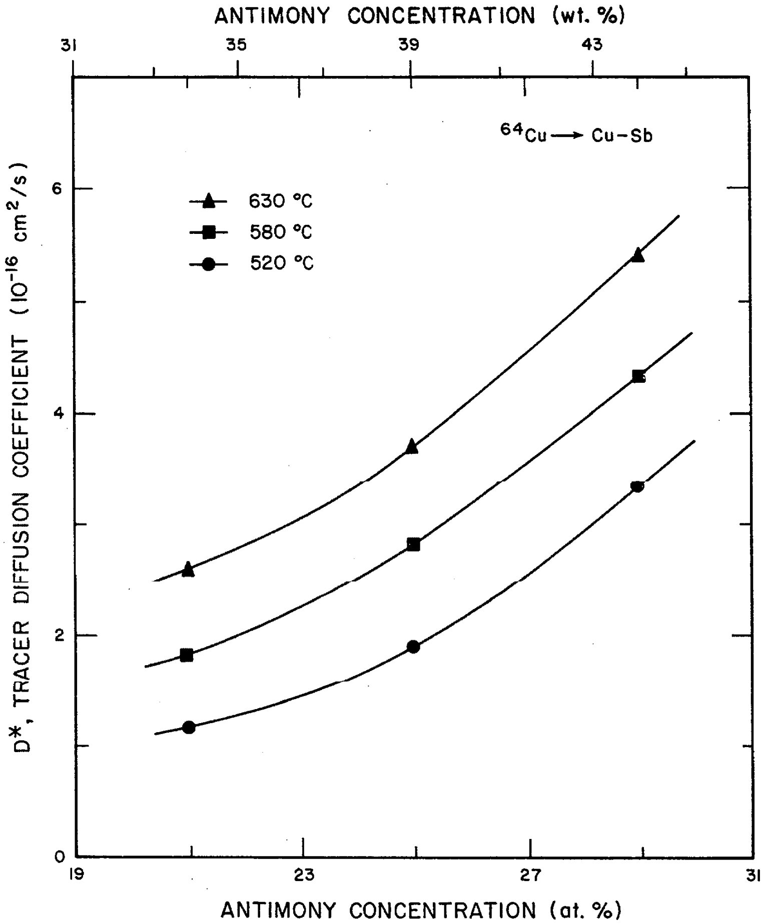

FIGURE 21. Tracer diffusion coefficients of ^{64}Cu in β-Cu_3Sb as a function of antimony concentration.

The plotted data points and curves are interpolated from the authors' original figure. Data from Heumann et al. [9].

crystals of GaSb. Similarily performed experiments with undoped p-type crystals yielded the same migration direction (toward the anode) for the radioactive copper. This migration behavior of copper is not typical and differs from what has been found for the electromigration of other group I and II impurities in III–V compounds.

The interdiffusion characteristics of the ternary system Cu-Ga-Sb was studied qualitatively by Kelly [22]. No interdiffusion coefficients were measured. In the experiment, a Cu-Ga(12.9 at.%) alloy was diffused against a Cu-Sb(1 at.%) alloy. After a diffusion anneal at 900 °C, visible "bands," normal to the direction of diffusion and parallel to the interface, were observed. A mathematical model based on the maximum rate of change in concentration of the diffusants was offered to describe the phenomena.

6.10. Cu-Sb-In

Studies in this ternary system have been limited to investigations [28, 29] concerned with the III–V semiconducting compound InSb and the diffusion of copper tracer atoms in it.

The first of these studies [28] utilized not only radiotracers, but also incremental sheet-resistivity techniques [30]. It was found that the measured diffusion coefficients were very structure-sensitive, as well as being dependent on specimen history. Single crystals of n-type (electron concentrations of 3×10^{14} to 1×10^{15} cm^{-3} at liquid-nitrogen temperatures) InSb and p-type (1×10^{15} cm^{-3} hole concentration) InSb yielded identical diffusion results. Radioactive ^{64}Cu was electroplated on (111) and (113) planes with no apparent effects on the diffusion behavior. The dislocation density in the plane surface was determined by counting

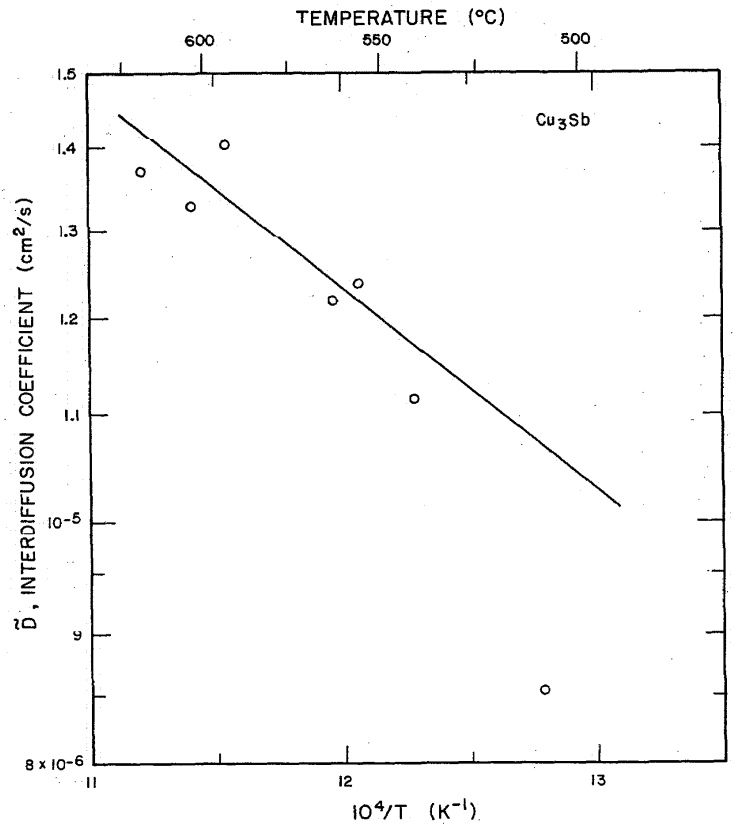

FIGURE 22. Interdiffusion coefficients in β-Cu_3Sb as a function of reciprocal absolute temperature.

The plotted data points and line are interpolated from the authors' original figure. Data from Heumann et al. [9].

etch pits. Diffusion annealing occurred over the temperature range 200–500 °C (±3 °C). The combination of both the incremental sheet-resistance and radioactive-tracer techniques revealed that copper has substitutional as well as interstitial properties in InSb, entering the crystal at a rapid interstitial rate and reacting readily with vacancies. In view of this non-Fickian behavior (e.g., figure 24), the data have to be interpreted in terms of four different diffusion mechanisms.

An "apparent" diffusion coefficient for Cu in InSb can be calculated for a dissociative diffusion process [31] in which both interstitial and substitutional copper take part. A plot of this "apparent" diffusion coefficient, $\bar{D}$, versus reciprocal temperature is shown in figure 25. This dissociative diffusion process has an activation energy of 1.08±0.08 eV, and a D_0 between 10^{-4} and 10^{-3} cm²/s. This dissociative mechanism is limited by vacancies diffusing in from the surface. The experimental points at the lower temperatures are relatively inaccurate because of the rather shallow *p-n* junctions obtained and the inhomogeneities in the starting-material resistivity. These experiments revealed that the apparent diffusion coefficient of copper in InSb is highly structure-sensitive (see figure 26, for example), as well as being dependent on the history of the specimens. Diffusion in crystals containing 10^5 dislocations/cm² is 5 orders of magnitude faster than in dislocation-free and annealed specimens. For the dislocation-free specimens, the following expression has been determined [32] and is applicable for the diffusion of ^{64}Cu impurities in InSb:

$$D_{\text{effective}}=9.0\times10^{-4}\exp(-1.08\ \text{eV}/kT)\ \text{cm}^2/\text{s}.$$

An "effective" diffusion coefficient for copper in InSb has also been determined [29]. Utilizing single crystals of *n*-type InSb (having an electron density $\approx 10^6/\text{cm}^3$, a mobility of $\approx 3\times10^5$ cm²/V·s at 77 K, and a dislocation density of $\approx 10^4/\text{cm}^2$), radioactive ^{64}Cu was diffused into the crystals at temperatures from 230 to 490 °C. The distribution of the ^{64}Cu was

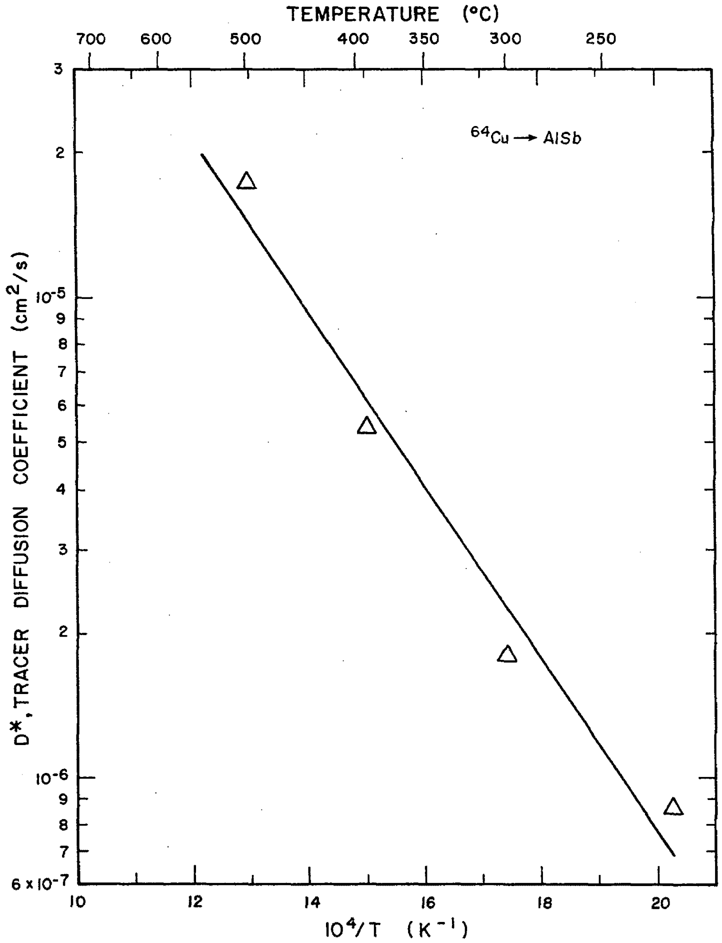

FIGURE 23. Tracer diffusion coefficients of ^{64}Cu in AlSb as a function of reciprocal absolute temperature.

Data from Wieber et al. [23].

determined by counting the activity in successive layers of the specimen, as well as by autoradiography. A complex concentration-dependence was found. Detailed study of the concentration dependence deep in the crystal could be described by a function close to the error function, and thus a diffusion coefficient could be calculated. Using the autoradiographic data, effective diffusion coefficients were determined and are plotted as a function of reciprocal temperature in figure 27. The temperature dependence of this diffusion can be expressed as:

$$D_{\text{effective}} = 3 \times 10^{-5} \exp(-0.37\ \text{eV}/kT)\ \text{cm}^2/\text{s}.$$

The results of these two investigations at first glance seem to differ—the latter study yielding tracer-impurity diffusion coefficients higher than the former. The values for the coefficients can be viewed as being in reasonable agreement when the dislocation densities and the accuracy of the measurements are considered.

The genuine diffusivity of substitutional copper in InSb has not been determined, but it is thought likely to be similar in order-of-magnitude to the self-diffusion of indium in InSb ($D_{\text{In}\rightarrow\text{InSb}} \cong 10^{-14}$ cm²/s at 480 °C) [33].

6.11. Cu-Sb-Zn

The diffusivity of ^{124}Sb in single crystals of Cu-Zn (β-brass: 47–48 at.% Zn) has been measured over the temperature range 351–594 °C by tracer sectioning techniques [34]. The diffusion coefficient is strongly dependent on the degree of long-range order at temperatures below 468 °C (the critical temperature) and only slightly dependent on the degree of short-range order at higher temperatures. The Arrhenius equation is obeyed only in the fully disordered phase, and the diffusion coefficient is given by:

$$D_{\text{Sb}}^* = 0.08 \exp(-23.5\ \text{kcal} \cdot \text{mol}^{-1}/RT)\ \text{cm}^2/\text{s}.$$

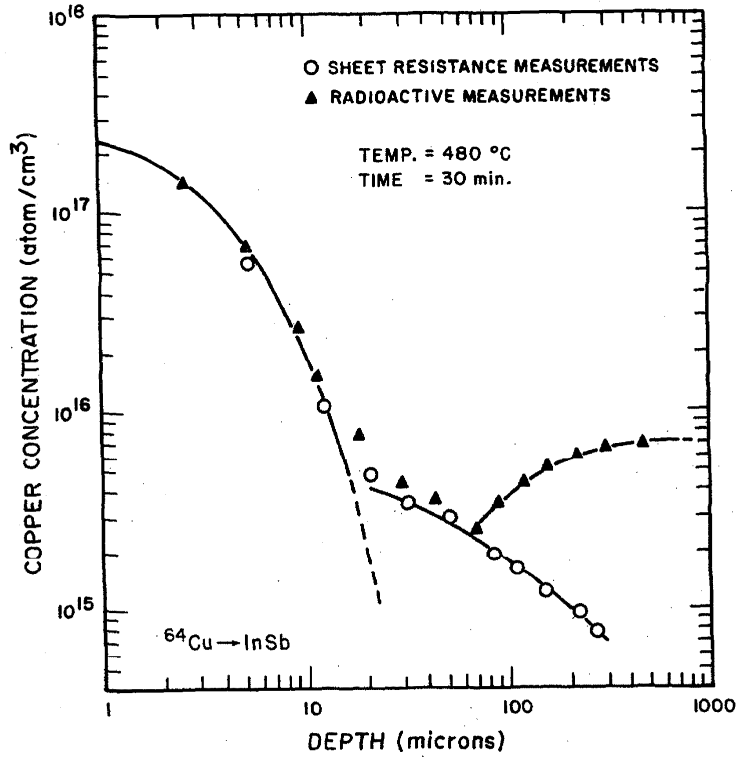

FIGURE 24. Distribution of ^{64}Cu in an InSb unannealed single-crystal sample at 480° C for 30 minutes analyzed by two different techniques.

Data from Stocker [28].

The temperature variation is seen in figure 28. The diffusion coefficients are estimated to be accurate to about $\pm 5\%$, with the major error being in the determination of the penetration depth. Some of the scatter in the data might also be attributed to the variation in the chemical composition in the specimens used.

When compared to the rates of diffusion of the other constituents, it was found that the antimony tracer diffuses at a rate greater than either copper or zinc in the disordered phase, and at a rate equal to that of the zinc in the ordered phase.

Some investigations [35–41] have found that radioactive-zinc diffusion in polycrystalline brass specimens is increased with antimony additions. All these investigations were of a qualitative nature, and no diffusion data were obtained.

6.12. Grain-Boundary Diffusion

The grain-boundary diffusion of ^{124}Sb in tracer amounts into 45° copper bi-crystals has been measured over the temperature range 605–720 °C [4]. Autoradiography was employed in making the quantitative measurements. The technique [3] follows the spread of the image of the diffusion zone (caused principally by the energy of the radioactive tracer) and then matches the experimental density-traces to computed curves. From the density maps of the grain-boundary region, concentration-distribution contours can be determined and grain-boundary diffusion coefficients calculated (using Suzuoka's mathematical exact solution for thin-source conditions). The grain-boundary width was assumed equal to 5×10^{-8} cm, and the grain-boundary diffusion coefficients are plotted versus the reciprocal absolute temperature in figure 29, and listed in table 9 along with some other pertinent numbers.

The straight line the author fits to his data is given by the expression:

$$D_{gb} = (23^{+20}_{-8}) \exp[-(21 \pm 3) \text{ kcal} \cdot \text{mol}^{-1}/RT] \text{ cm}^2/\text{s}.$$

The errors shown above (and in table 9) are the author's quoted values. Comparison of results obtained from two specimens annealed at the same temperature also indicates a measure of accuracy. With lower experimental temperatures, the combined errors increase markedly.

There is linearity in the Arrhenius plot over most of the temperature range, with a positive departure at

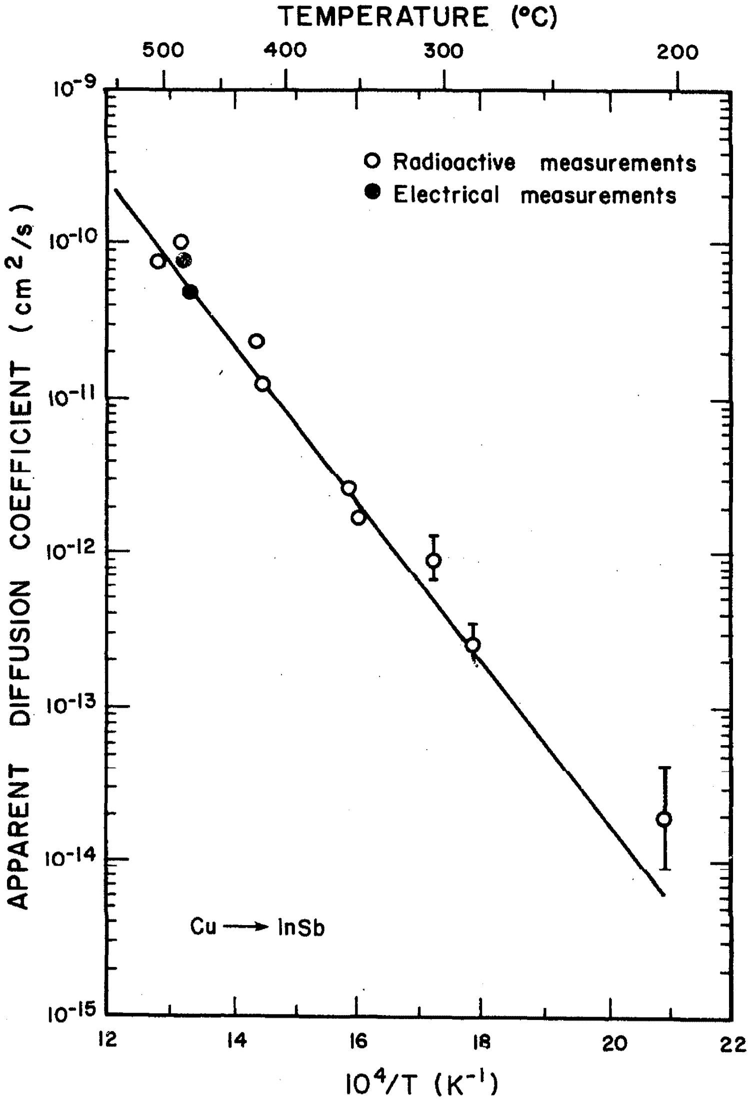

FIGURE 25. Apparent diffusion coefficients of copper in InSb from two types of measurements assuming a dissociative mechanism as a function of reciprocal absolute temperature.

Data from Stocker [28].

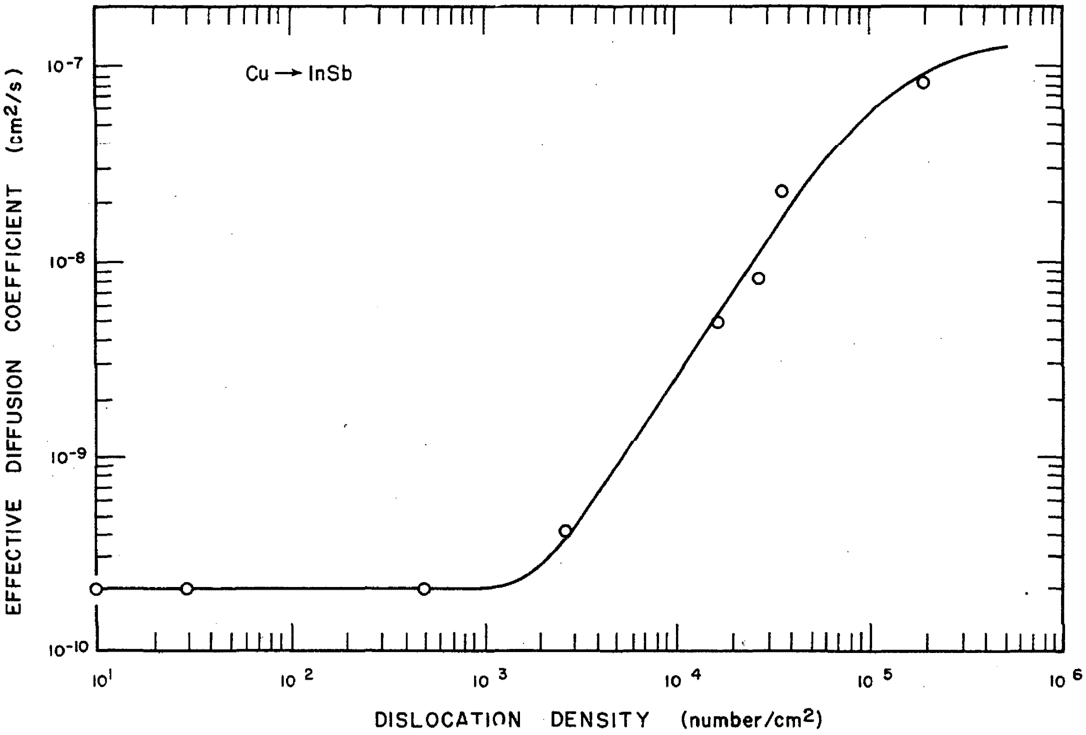

FIGURE 26. Effective diffusion coefficients of copper in InSb as a function of dislocation density.

Data from Stocker [28].

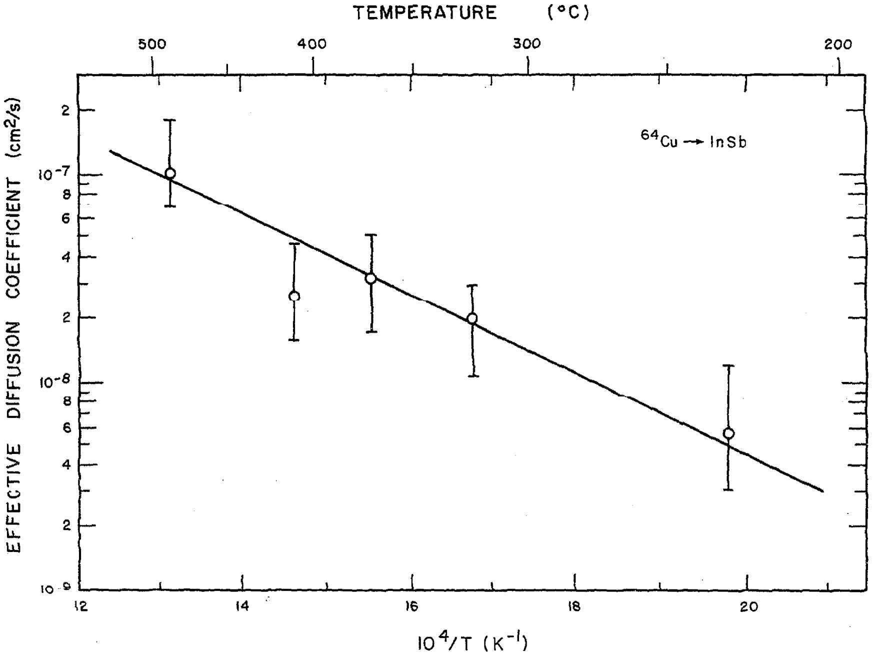

FIGURE 27. Effective diffusion coefficients of copper in InSb as a function of reciprocal absolute temperature.

Data from Boltaks and Sokolov [29].

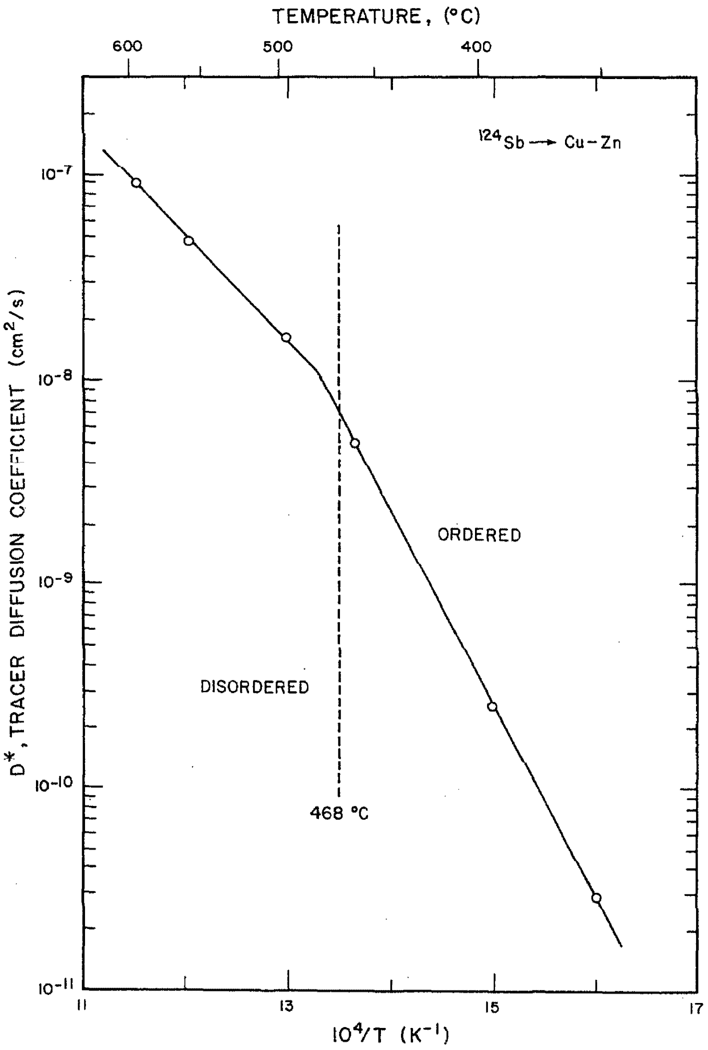

FIGURE 28. Tracer diffusion coefficients of ^{124}Sb in single crystal Cu-Zn (47–48 at.%) (β-phase) as a function of reciprocal absolute temperature.

Data from Kuper et al. [34].

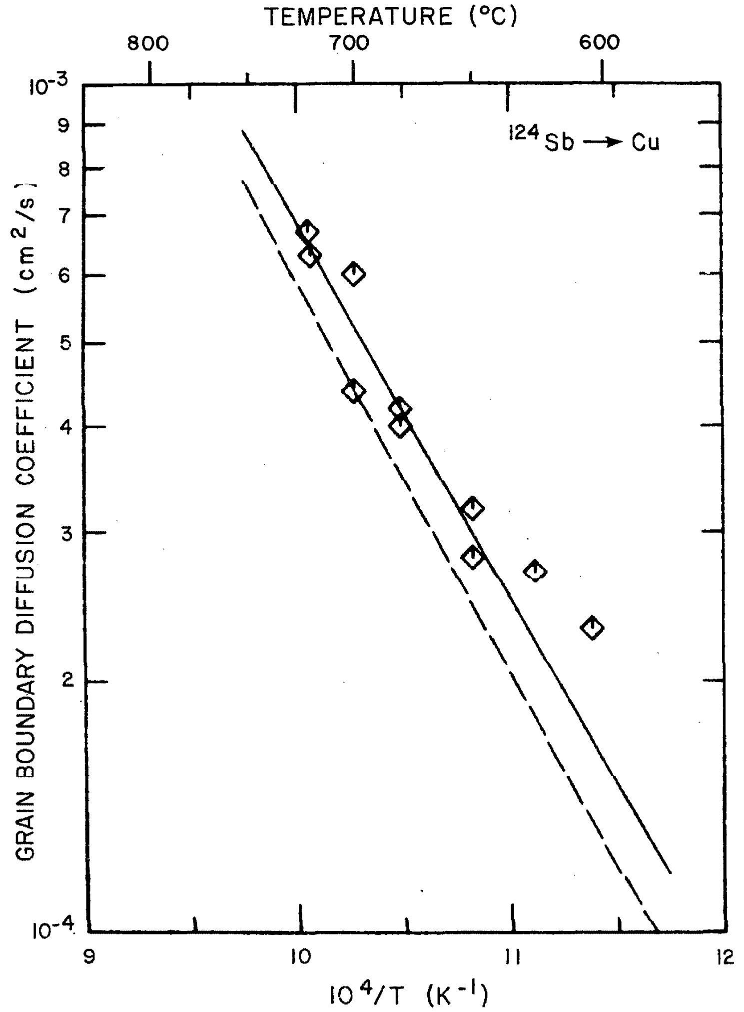

FIGURE 29. Grain-boundary diffusion coefficients of ^{124}Sb in pure copper as a function of reciprocal absolute temperature.

Copper bi-crystals with a misorientation of 45° supplied the grain boundary. The dashed line is Renouf's [4] stated line with $D_0=23$ cm²/s, and $Q=21$ kcal/mol. The solid line is a least-squares line with $D_0=16.2$ cm²/s, and $Q=20.0$ kcal/mol. His data points at 626 and 605 °C were not included in the calculation.

TABLE 9. Grain-boundary diffusion coefficients of ^{124}Sb in copper bi-crystals with a 45° misorientation. Data of Renouf [4].

T (°C)	D_{gb} (cm^2/s)	D_{gb}/D_{vol}
721	$(6.7 \pm 1.6) \times 10^{-4}$	3.0×10^6
720	$(6.3 \pm 1.6) \times 10^{-4}$	3.0×10^6
700	$(6.0 \pm 1.2) \times 10^{-4}$	5.0×10^6
	$(4.4 \pm 1.2) \times 10^{-4}$	3.5×10^6
680	$(4.2 \pm 1.2) \times 10^{-4}$	5.0×10^6
	$(4.0 \pm 1.2) \times 10^{-4}$	5.0×10^6
650	$(3.2 \pm 0.6) \times 10^{-4}$	8.2×10^6
	$(2.8 \pm 0.6) \times 10^{-4}$	7.3×10^6
626	$(2.7 \pm 0.8) \times 10^{-4}$	1.3×10^7
605	$(2.3 \pm 0.6) \times 10^{-4}$	1.9×10^7

the lowest temperatures. Reasons for this low-temperature enhancement are not known, although the results are consistent with experimental results he obtains for metals (^{110}Ag, ^{63}Ni) diffusing in copper grain-boundaries.

The grain-boundary diffusion of silver in copper antimony alloys is mentioned in section 6.6 on Cu-Sb-Ag alloys.

6.13. Electromigration

The electromigration of antimony impurities in copper has received attention from a number of investigators using a variety of techniques [2, 42–49]. All the data indicate that antimony was transported in the direction of the anode, and a variety of effective charge-numbers have been reported.

Although Kuzmenko and co-workers [42, 50] were able to calculate impurity diffusion coefficients for ^{124}Sb from their experimental data, they unfortunately relied on a comparison with some less reliable data (that of ref. 6) for determining their experimental temperatures.

Guilman and co-workers [49] followed the electromigration of radioactive ^{125}Sb in copper over the temperature range 850–985 °C, obtaining an activation energy of about 41 kcal/mol, in good agreement with the tracer data of Inman and Barr [1].

Hehenkamp [2, 47, 48, 51–54] has pointed out the importance of knowing the concentration dependence of the diffusion coefficient in electromigration studies involving the Cu-Sb system. He has shown that it is incorrect to assume constant migration velocities and concentration-independent mobilities in solid solutions containing as little as 0.1 at.% Sb. In his experiments, he has relied on the electron-probe microanalyzer to follow the electromigration of the elemental species, rather than a radioactive tracer.

Grimme [46] followed electromigration in Cu-Sb(0.3 at.%) alloys and obtained results consistent with those reported by Hehenkamp (see above).

In a resistometric study [43–45] of electromigration in dilute solid-solutions of Cu-Sb(1.0 at.%), the changes in solute concentration are determined by comparative resistance-measurements. An "effective" diffusion coefficient and an "apparent" activation energy were calculated. In their calculations, the authors [43] failed to note that for impurity diffusion the drift mobility does not reduce to 1/(correlation factor). Since large errors can be made if the Lidiard-LeClaire expressions for 1/(correlation factor) for impurity diffusion is substituted for the drift mobility [55], the calculated values of $q_{Sb}{}^*$ in this paper may be considerably in error.

In contrast to the above discussions dealing with terminal solid-solutions are the electromigration investigations in the β-phase (Cu_3Sb) undertaken by Heumann and Meiners [56]. Specimens containing 20.7 and 28.2 at.% antimony were subjected to currents of 1370–3132 A/cm^2 (temperature of 507–598 °C). Copper was transported to the cathode at very high rates, whereas the mobility of the antimony was very small—undetectable under the experimental conditions employed by the authors.

For a discussion of electromigration of ^{64}Cu in tellurium-doped and zinc-doped *n*-type GaSb crystals, see section 6.9 on Cu-Sb-Ga.

6.14. Thermomigration

The thermomigration of antimony impurities in copper has been the subject matter of several papers [47, 57]. Both groups found an enrichment of the Sb-impurity on the hot side and, therefore, negative apparent heats-of-transport. The size of this value is in question. Reasons for the discrepancy are not readily apparent, although it may be due in part to the experimental techniques (stationary redistribution of the Sb present in tracer amounts in a linear temperature gradient [57] versus an electron-microprobe determination of a steady-state profile [47]) and/or the contributions (e.g., model electronic, Thomson field, correlative effects, etc.) which make up the apparent heat-of-transport.

6.15. Strain-Enhanced Diffusion

Two experiments [5, 58] have been performed to determine the effect of strain on the tracer diffusion of ^{124}Sb into copper. Both found a negative result for the enhancement of tracer diffusivity with strain.

Inman [58] used polycrystalline tapered samples deformed in creep at 652 and 805 °C. The low strain rates used in his experiment probably would have not revealed any effect that might have been present. His results are summarized in table 10.

TABLE 10. The effect of tensile strain-rate on the ^{124}Sb tracer diffusion coefficients in copper. Data of Inman [58].

T (°C)	Strain Rate (10^{-7}/s)	D* (cm^2/s)
805	0	1.0×10^{-9}
	0.1	9.9×10^{-10}
	2.3	9.4×10^{-10}
652	0	4.4×10^{-11}
	0.4	6.5×10^{-11}
	1.0	4.7×10^{-11}
	1.6	6.4×10^{-11}
	5.0	5.2×10^{-11}

In the most-recent tracer study [5] single crystals of 99.99% pure electrolytic copper were grown in the shape of rectangular tensile specimens—the orientation of the crystals being such as to produce duplex slip from the beginning of strain. The results obtained are given in table 11, and plotted in figure 18 (see section 6.1).

TABLE 11. The effect of longitudinal strain-rate on the ^{124}Sb tracer diffusion coefficients in single crystal copper at 594 °C. Data of Barr et al. [5].

Strain Rate (10^{-6}/s)	D* (cm^2/s)
20	2.3×10^{-11}
4	6.9×10^{-12}
3	4.6×10^{-12}

Stress-enhanced interdiffusion in couples constructed of pure copper and antimony has been observed by Heumann and Heinemann [7] and by Behera and Brown [15]. The application of a compressive stress led to an apparent growth-rate in their multiphase diffusion couples at 390 °C.

The results are conflicting as to the role of the compressive stress in the nucleation of the phases Cu_2Sb and Cu_3Sb.

Heumann and Heinemann [7] found that with the application of pressures less than 570 psi (39.3 N/m^2, or pascals), only the Cu_2Sb phase formed in the interdiffusion zone. At pressures greater than 570 psi, a second phase, Cu_3Sb, formed. The Cu_3Sb phase formed after an incubation period and grew at a faster rate than the Cu_2Sb phase. A three-stage growth curve was observed for the phase Cu_3Sb.

Behera and Brown [15] repeated the above experiments at 390 °C and found that interdiffusion increases with stress, with the growth rate of the Cu_3Sb phase above the limiting stress of 400 psi (27.6 N/m^2, or pascals), approximately 70% greater than at zero psi. Electron-microprobe analysis and X-ray diffraction revealed the presence of Cu_3Sb and Cu_2Sb together in the interdiffusion zone. Both phases were present at the lowest applied stresses. Growth-rate curves indicated that diffusion was controlling at all stresses. No multi-stage growth curve was found for the phase Cu_3Sb.

Both groups observed a nucleation time for the Cu_3Sb phase, but Behera and Brown [15] found the time to be shorter and the nucleation occurring at much lower stresses than found by Heumann and Heinemann [7].

The disappearance of Cu_3Sb in a low-stress anneal following a high-stress anneal was found by both groups (although differing stresses are involved).

Kirkendall-marker experiments described in each of the papers [7, 15] indicated that copper was the diffusing atom.

It is difficult to assess the reasons for the discrepancies in results of the two groups. No doubt some of the differences may be attributed to the slightly differing experimental techniques. Heumann and Heinemann's diffusion anneals took place under semi-hydrostatic pressures, whereas Behera and Brown's applied loads were purely compressive (and stresses kept below 1000 psi (68.95 N/m^2, or pascals) to avoid creep).

6.16. Molten Metals

The diffusion of radioactive imputities (less than 5×10^{-4} at. %) of antimony in liquid copper over the temperature range 1100–1300 °C has been measured [59]. A modified capillary-reservoir method was employed as the experimental technique. The authors found (within the limits of their experimental errors) a linear relation between log D and $1/T$ and were able to calculate (using a least-squares method) an apparent activation energy and pre-exponential term. Their Arrhenius expression for the process is:

$$D^{\mathrm{liquid}}_{\mathrm{Sb}\rightarrow\mathrm{Cu}} = (2.5_5\times10^3)\exp[-(12.5\pm0.3)\ \mathrm{kcal\cdot mol^{-1}}/RT]\ \mathrm{cm^2/s}.$$

6.17. Cu-Sb References

[1] Inman, M. C., and Barr, L. W., "Diffusion of Antimony in Copper Single Crystals," Acta Metall. **8**, 112–116 (1960).

[2] Hehenkamp, Th., "Measurements of Transport Phenomena of Dilute Impurities in Metals," J. Appl. Phys. **39**, 3928–3930 (1968) [also presented at the Second National Conference on Electron Microprobe Analysis, Boston, June 14–16, 1967].

[3] Renouf, T. J., "The Measurement of Volume Diffusion by the Method of Autoradiography," Philos. Mag. **9**, 781–795 (1964).

[4] Renouf, T. J., "The Measurement of Grain Boundary Diffusion by the Method of Autoradiography," Philos. Mag. **22**, 359–375 (1970).

[5] Barr, L. W., Blackburn, D. A., and Brown, A. F., "Diffusion Rates in the Region Close to the Free Surface of a Metal," in *Radioisotopes in the Physical Sciences and Industry*, Vol. I (Proceedings of the Conference, Copenhagen, Sept. 6–17, 1960) (International Atomic Energy Agency, Vienna, 1962), pp. 137–157.

[6] Gertsriken, S. D., and Revo, A. L., "Investigation of the Effect of Small Admixtures of Tin and Antimony on the Parameters of Volume and Grain Boundary Diffusion of these Elements into Copper," (in Ukrainian) Ukr. Fiz. Zh. **6**, 398–407 (1961) [translation available from NTIS as TT 70–57086].

[7] Heumann, Th., and Heinemann, F., "Multiphase Diffusion in the Copper-Antimony System," (in German) Z. Elektrochem. **60**, 1160–1169 (1956) [translation available from NTC as TT 70–57545].

[8] Steigman, J., Shockley, W., and Nix, F. C., "The Self-Diffusion of Copper," Phys. Rev. **56**, 13–21 (1939).

[9] Heumann, Th., Meiners, H., and Stuer, H., "Determination of the Cu Diffusion Coefficient in the High Temperature Beta-Phase of the Cu-Sb System," (in German) Z. Naturforsch. A **25**, 1883–1891 (1970).

[10] Gruzin, P. L., "Application of Artificial Radioactive Tracers for Studying Diffusion and Self-Diffusion in Alloys," (in Russian) Dokl. Akad. Nauk SSSR **86**, 289–292 (1952) [translation available from NTIS as TT 70–57022].

[11] Weiss, M. H., "Introduction to the Study of the Concentration of Metals," (in French) Rev. Metall. (Paris) **21**, 18–41 (1924).

[12] Weiss, H., and Lafitte, P., "The Interpenetration in Solids," (in French) C. R. Acad. Sci. **173**, 146–148 (1921) [translation available from NTC as TT 70–57756].

[13] Weiss, H., "Introduction to the Study of Metallic Cementation," (in French) Ann. Chim. **19**, 201–212 (1923) [translation available from NTC as TT 71–55270].

[14] Boettcher, A., and Thun, R., "Phase Transformation in the System Copper-Antimony," (in German) Z. Anorg. Chem. **283**, 26–48 (1956) [translation available from NTC as TT 70–57800].

[15] Behera, S. K., and Brown, L. C., "Stress Enhanced Diffusion in Cu-Sb Diffusion Couples," Metall. Trans. **1**, 1032–1034 (1970).

[16] Heumann, Th., "New Observations on the Kirkendall Effect and Electrolytic Transport in Solid Alloys," (in French) in *La Diffusion Dans Les Metaux*, edited by J. D. Fast, H. G. Van Bueren and J. Philibert (Bibliotheque Technique Philips, Eindhoven, 1957) pp. 59–75 [translation available from NTC as TT 71–55208, *Diffusion in Metals*].

[17] Heumann, Th., "The Calculation of Diffusion Coefficients in Cases of Single-phase and Multiple-phase Diffusion in Solid Alloys," (in German) Z. Phys. Chem. (Leipzig) **201**, 168–189 (1952) [translation available from NTC as NTC II–73].

[18] Arkharov, V. I., and Gol'dshtein, T. Yu., "On the Frontal Diffusion of Ag in Several Polycrystalline Metals," (in Russian) Tr. Inst. Fiz. Met. Akad. Nauk SSSR Ural. Fil., No. 11, 81–89 (1950) [translation available from NTIS as TT 70–58186].

[19] Arkharov, V. I., and Gol'dshtein, T. Yu., "Effects of Small Amounts of Impurities on the Process of Dissociation of a Super Saturated Solid Solution," (in Russian) Tr. Inst. Fiz. Met. Akad. Nauk SSSR Ural. Fil., No. 11, 104–113 (1950) [translation available from NTIS as TT 70–57078].

[20] Arkharov, V. I., and Pentina, A. A., "Investigation of the Effect of Relative Crystal Orientation on Phenomena Occurring at Grain Boundaries. II. The Effect of Mutual Crystallites Orientation on the Concentration Distribution Irregularity of the Surface-Philic Admixture of Antimony to Copper," (in Russian) Fiz. Met. Metalloved. **5** (1) 68–73 (1957) [Phys. Met. Metallogr. **5** (1) 52–56 (1957)].

[21] Arkharov, V. I., and Pentina, A. A., "A study of Effect of the Mutual Orientation of Crystals on Intercrystalline Diffusion and Internal Adsorption," (in Russian) in *Issledovaniya Po Zharoprochnym Splavam*, Vol. 3, edited by I. P. Bardin, G. V. Kurdyumov, et al. (Izdatel'stvo Akad. Nauk SSSR, Moscow, 1958), pp. 208–246 [translation available from NTIS as AD 418153, *Investigation of Heat Resistant Alloys*].

[22] Kelly, D. P., *A Study of Counterdiffusion in Copper Alloys*, Ph.D. Thesis, Univ. Cincinnati (1962) 48 pp.

[23] Wieber, R. H., Gorton, H. C., and Peet, C. S., "Diffusion of Copper into AlSb," J. Appl. Phys. **31**, p. 608 (1960).

[24] Sirca, F., "Influence of Alpha Forming Elements on the Diffusion of Copper in Gamma-Iron," (in French) Mem. Sci. Rev. Metall. **57** (11) 879–887 (1960) [translation available from NTC as TT 70–57918].

[25] Sirca, F., "Influence of Alpha Forming Elements on the Diffusion of Copper into Gamma-Iron, Part II.," (in Slovenian) Rud. Met. Zb., No. 4, 377–387 (1961) [translation available from NTC as TT 70–56048].

[26] Blashku, A. I., and Dzhafarov, T. D., "Influence of Tellurium and Zinc on the Diffusion and Solubility of Copper in GaSb," (in Russian) Fiz. Tverd. Tela **15**, 769–771 (1973) [Sov. Phys.-Solid State **15**, 536–537 (1973)].

[27] Vlashku, A. I., Burdiyan, I. I., and Dzhafarov, T. D., "Electrotransport of Copper in GaSb," (in Russian) Fiz. Tverd. Tela **15**, 1508–1511 (1973) [Sov. Phys.-Solid State **15**, 1012–1014 (1973)].

[28] Stocker, H. J., "Diffusion, Solubility and Electrical Properties of Copper in Indium Antimonide," Phys. Rev. **130**, 2160–2169 (1963).

[29] Boltaks, B. I., and Sokolov, V. I., "Diffusion of Gold in Indium Antimonide," (in Russian) Fiz. Tverd. Tela **6**, 771–775 (1964) [Sov. Phys.-Solid State **6**, 600–603 (1963)].

[30] Reiss, H., and Fuller, C. S., "Diffusion Processes in Germanium and Silicon," Chapter 6 in *Semiconductors*, edited by N. B. Hannay (Reinhold Publishing Corp., New York, 1959) pp. 222–268.

[31] Frank, F. C., and Turnbull, D., "Mechanism of Diffusion of Copper in Germanium," Phys. Rev. **104**, 617–618 (1956).

[32] Gertsriken, S., and Faingol'd, M., "The Calculation of the Diffusion Coefficient in Mixtures of Powdered Substances," (in Russian) Zh. Tech. Fiz. **10**, 574–577 (1940) [translation available from Brit. Iron Steel Inst. as BISI 308].

[33] Rosi, F. D., Meyerhofer, D., and Jensen, R. V., "Properties of *p*-Type GaAs Prepared by Copper Diffusion," J. Appl. Phys. **31**, 1105–1108 (1960).

[34] Kuper, A. B., Lazarus, D., Manning, J. R., and Tomizuka, C. T., "Diffusion in Ordered and Disordered Copper-Zinc," Phys. Rev. **104**, 1536–1541 (1956).

[35] Hopkin, L. M. T., "A Note on the Effect of Antimony on Hole Formation during the Diffusion of Zinc from Brass in Vacuo," J. Inst. Met. **85**, 422–424 (1956–57).

[36] Hopkin, L. M. T., "Effect of Stress of Hole Formation during the Diffusion of Zinc from Brass in Vacuo," Nature (Lond.) **180**, p. 808 (1957).

[37] Gertsriken, S. D., Geller, A., and Trofimenko, V., "Effect of a Third Element on the Diffusion Coefficient of Zinc in α-Brass," (in Ukrainian) Izv. Sekt. Fiz.-Khim. Anal. Inst. Obshch. Neorg. Khim., Akad. Nauk SSSR **16**, 174–179 (1943) [translation available from NTIS as TT 70–57077].

[38] Accary, A., "The Influence of Impurities on the Rate of Diffusion in α-Brass," (in French) C. R. Acad. Sci. **241**, 1301–1304 (1955) [translation available from NTC as TT 71–21377].

[39] Accary, A., "Micrographic Study of the Influence of Impurities on Diffusion in Alpha Brass," (in French) C. R. Acad. Sci. **241**, 1763–1765 (1955).

[40] Accary, A., "Investigation of the Diffusion in α-Brasses Using Methods Depending on the Evaporation or Condensation of Zinc," (in French) in *Colloque Sur La Diffusion A L'Etat Solide* (Proceedings of the Conference on Solid State Diffusion, Saclay, July 1958) (North-Holland Publishing Co., Amsterdam, 1959) pp. 45–55 [also available as Comm. Energ. At. (Fr.) Rapp. No. 1292 (1959) 11 pp.] [translation available from NTC as TT 71–55282].

[41] Accary, A., *Study of Diffusion in Alpha Brass by Means of Evaporation and Condensation of Zinc. Influence of Diffusion Direction and the Presence of Impurities*, (in French) Ph.D. Thesis, Univ. Paris (1957) 42 pp. (also available as CEA Rpt. No. 759) [translation available from NTC as TT 70–57557].

[42] Kuz'menko, P. P., Ostrovskii, L. F., and Koval'chuk V. S., "Mobility of Sb, Fe, Co in Copper," (in Russian) Fiz. Tverd. Tela **4**, 490–493 (1962) [Sov. Phys.-Solid State **4**, 356–358 (1962)].

[43] Stepper, H.-J., and Wever, H., "Electrodiffusion in Dilute Copper Alloys," J. Phys. Chem. Solids **28**, 1103–1108 (1967).

[44] Stepper, H.-J., and Wever, H., "Electrotransport of Sn, Sb, and Ni in Copper," Abst. Bull. Trans. AIME **2**, p. 8 (1967).

[45] Stepper, H.-J., *A Method for Evaluating Electrolytic Transfer by Small Impurities in Copper Based on Resistivity Measurements*, (in German) Ph.D. Thesis, Technischen Univ. Berlin (1965), 83 pp. [translation available from NTC as TT 70–58156].

[56] Grimme, D., "The Influence of Impurities on Electrotransport in Copper," Chapter 2.3 in *Atomic Transport in Solids and Liquids* (Proceedings of the Conference, Marstrand, Sweden, June 15–19, 1970) edited by A. Lodding and T. Lagerwall (Verlag der Zeitschrift fur Naturforschung, Tubingen, 1971) pp. 65–67.

[47] Hehenkamp, Th., "Electro- and Thermotransport of Impurities of Copper and Silver," Chapter 2.4 in *Atomic Transport in Solids and Liquids* (Proceedings of the Conference, Marstrand, Sweden, June 15–19, 1970) edited by A. Lodding and T. Lagerwall (Verlag der Zeitschrift fur Naturforschung, Tubingen, 1971) pp. 68–72.

[48] Hehenkamp, Th., "Determination of the Charge of the Foreign Atoms in Dilute Solution through Microprobe Measurements of the Material Transport in Metals," (in German) Mikrochim. Acta [Wein] Suppl. **4**, 147–156 (1970) [translation available from NTC as TT 72–53181].

[49] Guilmin, P., Turban, L., and Gerl, M., "Electrotransport of Impurities in Copper and Nickel," (in French) J. Phys. Chem. Solids **34**, 951–959 (1973).

[50] Kuz'menko, P. P., Ostrovskii, L. F., and Koval'chuk, V. S., "Mobility of Small Tin Impurities in Copper and Silver," (in Russian) Fiz. Met. Metalloved. **13** (3) 406–410 (1962) [Phys. Met. Metallogr. **13** (3) 83–87 (1962)].

[51] Hehenkamp, Th., Ph.D. Thesis, Munster Univ. (1966).

[52] Hehenkamp, Th., "Microprobe Measurements of the Matter Transport in Solid Metals," (in German) Mikrochim. Acta [Wien] Suppl. 3, 79–90 (1968).

[53] Hehenkamp, Th., Verh. Dtsch. Physik. Ges. (VI) **4**, p. 74 (1969).

[54] Hehenkamp, Th., "Study of Point Defects in Metals by Electro- and Thermotransport," in *Vacancies and Interstitials in Metals* (Proceedings of the Conference, Julich, Sept. 23–28, 1968) (North-Holland Publishing Co., Amsterdam, 1969) pp. 91–122.

[55] Manning, J. R., "Drift Mobility and Diffusion for Impurities in Ionic Crystals," Phys. Rev. **A 139**, 2027–2034 (1965).

[56] Heumann, Th., and Meiners, H., "Electrotransport in the β-Phase of the Copper-Antimony System," (in German) Z. Metallkd. **64**, 105–110 (1973).

[57] Schroerschwarz, R., and Heitkamp, D., "Thermotransport of Substitutional Impurities in Copper," Phys. Status Solidi **B 45**, 273–286 (1971).

[58] Inman, M. C., Comment on "Point Defects and the Mechanical Properties of Metals and Alloys at High Temperatures," by McLean, D., in *Vacancies and Other Point Defects in Metals and Alloys* (A symposium held at the Atomic Energy Research Establishment, Harwell, Berks., Dec. 10, 1957) (The Institute of Metals, London, 1958) Institute of Metals Monograph and Report Series No. 23, pp. 224–228.

[59] Ejima, T., and Yamamura, T., "Impurity Diffusion in Liquid Copper and Silver," in *Conference on the Properties of Liquid Metals* (Proceedings of the 2nd International Conference Tokyo, Japan, Sept. 3–8, 1972) (Taylor and Francis Ltd., London, 1973) pp. 537–541.

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