RECEIVED BY DTIC SEP 13 1968

COO-1198-559

MASTER

THE THERMOMIGRATION OF AU¹⁹⁵ AND SB¹²⁵
IN GOLD AND NI⁵⁹ IN NICKEL

Willis Mock, Jr.

Department of Physics and Materials Research Laboratory

University of Illinois, Urbana, Illinois

October 1968

This is a technical information document based on a thesis submitted by Willis Mock, Jr. in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics in the Graduate College of the University of Illinois 1968. The research was supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-1198.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THE THERMOMIGRATION OF Au^{195} AND Sb^{125}
IN GOLD AND Ni^{59} IN NICKEL

Willis Mock, Jr., Ph.D.
Department of Physics
University of Illinois, 1968

COO--1198-559

DE84 017367

The effect of large thermal gradients on the mass transport of Au^{195} and Sb^{125} in gold and Ni^{59} in nickel has been investigated. Specimens in the form of rods containing two welded interfaces separated by 1/8-inch were fabricated. Each interface contained a layer of the appropriate tracer and an inert radioactive $\text{Hf}^{181}\text{O}_2$ marker. The specimens were annealed in a vacuum furnace which provided a temperature gradient of approximately $300^\circ\text{C}/\text{cm}$. The radioactive penetration profiles at the hot and cold interfaces were determined experimentally by sectioning the specimen on a lathe and assaying the radioactivity in each section. The penetration profiles, which were skewed gaussians, were curve fit by the method of least squares. The temperature at each interface and the temperature gradient were determined from the measured D values and the known tracer self-diffusion coefficient.

During the temperature gradient anneal the maximum of the tracer profile at the hot interface shifted with respect to the $\text{Hf}^{181}\text{O}_2$ marker. Using the measured shift values, the heat of transport of Au^{195} in gold was measured to be $Q_{\text{Au}}^* = 0.80 \pm 0.27 \text{ eV}$. This value supports Huntington's theory of the thermomigration of solvent atoms in single band metals.

The theory predicts that the static temperature gradient contribution to

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

the heat of transport is approximately equal to the atomic migration energy and is two orders of magnitude larger than the thermoelectric field and charge carrier-ion interaction effects.

The heat of transport of Ni^{59} in nickel was estimated to be $Q_{\text{Ni}}^* = 1.3 \pm 7.2$ eV. Because the measured value for the shift was within the experimental error, a large uncertainty in Q_{Ni}^* resulted. It is therefore not possible to draw conclusions concerning the magnitude of the charge carrier-ion interaction.

The experimentally determined value of the Sb^{125} heat of transport in gold was found to be $Q_{\text{Sb}}^* = -2.02 \pm 0.23$ eV. According to Gerl's theory for dilute impurity thermomigration, this large negative number indicates that the charge carrier-impurity ion interaction is the dominant driving force for Sb^{125} impurity thermomigration in gold, because the cold electrons moving up the temperature gradient impart more momentum to the impurity atom than the hot electrons moving down the temperature gradient. Q_{Sb}^* compares favorably with the theoretically calculated value for the heat carrier-impurity ion interaction of $Q^* = -0.5$ eV for antimony thermomigration in silver.

ACKNOWLEDGEMENTS

The author wishes to thank his advisor, Professor David Lazarus, for his guidance and encouragement throughout this thesis. Also, he would like to thank Dr. W. D. Seward and Dr. D. Gupta for helpful discussions. Finally, the author is grateful to his wife for typing the rough draft of this thesis and for her general encouragement throughout this project.

The research support of the United States Atomic Energy Commission is also gratefully acknowledged.

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. PHENOMENOLOGICAL EQUATIONS	8
A. Tracer Self-Thermomigration	8
B. Dilute Substitutional Impurity Thermomigration	14
III. EXPERIMENTAL PROCEDURE	18
A. Specimen Preparation	18
B. Radioactive Isotope Application	18
C. Welding Apparatus	22
D. Thermomigration Apparatus	27
E. Sectioning Procedure	33
F. Weighing and Counting Procedure	34
IV. ANALYSIS OF EXPERIMENTAL RESULTS	36
A. Method Used to Curve Fit a Tracer Profile	36
B. Interface Temperature Measurement and Calculation of Dt Values	39
C. Shift of Gold Tracer	44
D. Shift of Antimony Tracer	55
E. Shift of Nickel Tracer	55
V. DISCUSSION OF RESULTS	74
A. Comparison of Self-Thermomigration Results with Theory	74
B. Comparison of the Antimony Impurity Thermomigration Result with Theory	78
VI. SUMMARY AND CONCLUSIONS	82
BIBLIOGRAPHY	84
VITA	85

I. INTRODUCTION

If a homogeneous binary alloy is placed in a temperature gradient a redistribution of the constituents can occur with one constituent migrating to the cold end of the specimen and the other migrating to the hot end. This phenomenon, which is called thermomigration, was first investigated by Ludwig^{1/} and Soret^{2/} in gases and liquids. Only recently has the phenomenon been investigated in solids.

The basic macroscopic equations governing the phenomenon in solids are obtained from irreversible thermodynamics and have been discussed by several authors.^{3,4/} For a pure solid containing vacancies the flux of vacancies with respect to the lattice in one dimension along the temperature gradient is given by

$$J_v = \frac{n_v D_v}{kT^2} (Q^* - \Delta H_F) \frac{dT}{dx} \quad (1)$$

Here D_v is the vacancy diffusion coefficient, ΔH_F is the vacancy formation enthalpy, n_v is the local equilibrium vacancy concentration, T is the absolute temperature, $\frac{dT}{dx}$ is the temperature gradient, k is Boltzmann's constant, and Q^* is the heat of transport of the solvent atoms. The heat of transport is defined as the flux of heat transported by a unit mass current at constant temperature:

$$Q^* = \left(\frac{J_q}{J_m} \right) \frac{dT}{dx} = 0 \quad (2)$$

Here J_q is the flux of heat associated with the flux, J_m , of atoms of

mass m . In a single component system, to conserve lattice sites, $J_m = -J_v$. The net current of vacancies through the crystal lattice will be toward higher temperatures if $Q^* - \Delta H_F$ is positive and toward lower temperatures if $Q^* - \Delta H_F$ is negative, whereas the net flow of atoms will be in the opposite direction. The net flux of atoms through the crystal gives rise to a motion of markers fixed to the crystal lattice with respect to the laboratory frame since lattice planes are created at one part of the crystal and destroyed at another. The markers will move in a direction opposite to that of the net current of atoms.

In the past, two methods for measuring the velocity of the crystal lattice have been used. One method^{5/} consists of placing scratch marks on the specimen perpendicular to the temperature gradient and observing the relative motion of the marks with a microscope. The quantity $Q^* - \Delta H_F$ is determined from the relative distance change between the marks. This method suffers from at least two adverse effects. It is possible that the marks act as sources and sinks for vacancies in such a way that the observed net mass transport as measured by the marker movement is actually less than the actual mass transport which occurred. Another possible source of error is that surface diffusion effects taking place in the region of the scratch marks may govern their motion, rather than volume diffusion effects.

The second method^{6/} for measuring the lattice movement is to sinter small inert wires into the volume of the crystal and observe the change in distance between the wires. The largest source of error in this method is improper bonding between the inclusion wires and the specimen, with the result that the wires do not move with the velocity of

the lattice. In addition, void growth and strain effects around the wire may influence the wire movement. These experimental errors are reflected in the results reported for $Q^* - \Delta H_F$ using these two methods. Positive, zero, and negative values for $Q^* - \Delta H_F$ have all been reported in the literature by different experimenters for both copper and zinc. In these and in other metals the errors reported could be as large as 100%.

A more accurate method for measuring the heat of transport would obviously be desirable. Such a method exists and has been used for electromigration and Kirkendall effect experiments. This is the method of internal radioactive markers and tracers. In this method the net flux of atoms with respect to the lattice is measured using radioactive isotopes. A thin layer of radioactive tracer is deposited on one surface of mating optical flats. The other surface is coated with an exceedingly small concentration of non-diffusing internal radioactive marker ($< 1/10$ atom layer). The flats are placed in contact and welded together in a vacuum. Then the welded specimen is placed in a temperature gradient for the diffusion anneal. During the anneal the maximum of the tracer profile shifts with respect to the non-diffusing internal marker. The specimen is then sectioned on a precision lathe to determine the penetration profile of the tracer and the shift with respect to the internal marker.

This method has advantages over the previous two methods: first, the net flux of atoms through the bulk of the specimen is measured directly and is not affected by surface abnormalities; second, the internal marker which is used to mark the position of the lattice is a

thin layer of radioactive isotope, and this would not introduce strain effects and vacancy precipitation as would an internal foreign body.

In the present experiment the thermomigration of Au^{195} and Sb^{125} in gold and Ni^{59} in nickel has been measured. The Au^{195} in gold thermomigration experiment was undertaken because no self-consistent data for gold self-thermomigration exists. Adda et al.,^{7/} using the method of marking the crystal lattice internally with a thin wire, observed no relative motion between the wire and a thin plate which marked the laboratory frame, indicating that $Q^* - \Delta H_F \approx 0$. Meehan and Lehman^{6/} obtained a value of -0.20 ± 0.15 eV for $Q^* - \Delta H_F$ using internal wires. But they stressed that their result should be viewed qualitatively, since in a second specimen a smaller marker movement was observed, while for a third specimen no marker movement was observed at all. They attributed the above-mentioned errors as probably causing the different results for the three specimens. Jaffe and Shewmon^{5/} using the scratch mark technique obtained a value for $Q^* - \Delta H_F$ of -0.37 eV, although it seems that this value should be decreased by about 20% because the diffusion correlation factor, f , was apparently neglected. Due to the inconsistency of these results, an accurate determination of self-thermomigration in gold is clearly desirable, since other defect properties of gold have received careful study.

No previous results for the thermomigration of Sb^{125} in gold or Ni^{59} in nickel have been reported. These data, as well as the results for self-thermomigration in gold are essential to test atomistic theories for thermomigration which have been proposed by Huntington,^{8/} Gerl,^{9/} and others.^{10,11/}

In these models it is presumed that a solvent atom situated at the saddle-point position in a temperature gradient will experience three driving forces: a force due to the static temperature gradient, a force due to the thermoelectric field, and a force due to the heat carrier interaction. For single band metals the contribution due to the heat carrier interaction is presumed negligible; because, to maintain current neutrality, the flow of electrons or holes serving as heat carriers down the temperature gradient must be balanced by an equal flow of less energetic electrons or holes up the temperature gradient. The result is that the net interaction with moving charges should be small. For multi-band metals the zero charge flow condition can also be satisfied with both holes and electrons flowing down the temperature gradient. The charge carrier interaction can therefore be enhanced considerably. The force due to the static temperature gradient is the same order of magnitude for both single band and multiband metals. Thus by measuring self-thermomigration in gold, which is a single band conductor, and in nickel, which is a multiband conductor, this theory can be tested. The heat carrier interaction is also predicted to be significant for substitutional solute impurities with a valence different from the solvent. This results from the large scattering cross section of the impurity for charge carriers. Antimony (valence 5) thermomigration in gold (valence 1) is therefore a good choice to test this part of the theory.

Huntington has derived the following expression for the heat of transport of solvent atoms in single band metals:

$$Q^* = \alpha \beta \Delta H_m + eZ\eta T + \frac{(\pi kT)^2}{6\epsilon_F} (n_e l \sigma_i) \quad , \quad (3)$$

where the three terms on the right-hand side of the equation are due to the above-mentioned forces. The first term is the contribution due to the static temperature gradient; it has been determined using the Wirtz^{12/}-Brinkman^{13/} model. This model predicts that

$$Q_1^* = \alpha \beta \Delta H_M ; \quad (4)$$

ΔH_M is the vacancy migration energy, α is an enhancement factor which is due to the fact that a phonon scattered by a vacancy will enhance the temperature gradient slightly, and β is a fraction which is predicted to about 0.8 or 0.9. A jumping atom is assumed to carry an energy $\beta \Delta H_M$ forward in the jump direction when it moves into a vacant site; the remainder of the migration energy, $(1 - \beta) \Delta H_M$, is presumed localized in the motion of the saddle-point atoms. β is thus a measure of the distribution of the migration energy between normal modes when a jump occurs. Since α is approximately unity, Q_1^* is expected to be of the order of the migration energy.

The contribution due to the thermoelectric field is

$$Q_2^* = e Z \eta T , \quad (5)$$

where e is the magnitude of the electronic charge, Z is the charge number of the moving ion seen by the electrostatic field, η is the Thompson coefficient, and T is the absolute temperature. It has been difficult to predict a value for Z theoretically since it is a function of conduction electron screening. At ordinary diffusion temperatures Q_2^* is estimated to be smaller than 0.01 eV and thus is negligible compared to Q_1^* .

The contribution due to the charge carrier-ion interaction for a single band metal is given by the last expression in Eq. (3). ϵ_F is the Fermi energy, n_e is the electron concentration, ℓ is the mean free path for electrons, and σ_i is the scattering cross section for electrons by the activated complex. Huntington estimates this term to be less than 0.02 eV at diffusion temperatures for single band metals.

For the two band metal a more complex expression is obtained for the charge carrier-ion interaction contribution to the heat of transport,

$$Q_3^* = -eTS \left(\frac{1+\gamma}{1-2\gamma} \right) (1 + 3\delta) (n_e \sigma_i \ell) \quad (6)$$

Here S is the absolute thermoelectric power and γ and δ are ratios of energy integrals involving hole band contributions to electron band contributions. Q_3^* has been estimated to be as large as 1 eV.

In summary, it is predicted theoretically that the heat of transport for solvent atoms in single band metals should depend almost entirely on the static temperature gradient contribution which is of the order of magnitude of the migration energy. For solvent atoms in multi-band metals, the heat of transport is expected to consist of two terms: the static temperature gradient contribution of the order of magnitude of the migration energy, plus an equally important contribution due to the heat carrier-ion interaction which is expected to be of the order of an electron volt.

II. PHENOMENOLOGICAL EQUATIONS

This chapter is devoted to the development of the flux equations for tracer self-thermomigration and dilute impurity substitutional thermomigration. From the flux equations expressions are obtained for the shift of the tracer profile maximum with respect to the lattice marker. The development follows the theory as discussed by Lazarus^{14/} for tracer self-diffusion and by Adda^{4/} for thermomigration.

A. Tracer Self-Thermomigration

Let A represent the solvent atoms and A* represent the tracer atoms. Diffusion only along the x-direction is considered. The general expressions for the flux of tracer atoms (A*) and solvent atoms (A) in the lattice frame are given by^{4/}

$$J_{A^*} = -D_{A^*} \frac{\partial n_{A^*}}{\partial x} - [L_{A^*A^*}(Q_{A^*}^* - \Delta H_F) + L_{A^*A}(Q_A^* - \Delta H_F)] \frac{1}{T} \frac{dT}{dx} ; \quad (7)$$

$$J_A = +D_A \frac{\partial n_{A^*}}{\partial x} - [L_{AA^*}(Q_{A^*}^* - \Delta H_F) + L_{AA}(Q_A^* - \Delta H_F)] \frac{1}{T} \frac{dT}{dx} . \quad (8)$$

Since the tracer and solvent atoms are chemically equivalent, $Q_{A^*}^* = Q_A^*$. The L's are the phenomenological coefficients relating the fluxes to the driving forces of chemical potential gradient and temperature gradient.

Let n_{A^*} , n_A , n_v , and n represent the concentrations of tracer atoms, solvent atoms, vacancies, and lattice sites respectively. These are related by the equation

$$n_A + n_{A^*} + n_v = n . \quad (9)$$

Since at constant temperature the total current $J_{A^*} + J_A = 0$, the coefficients D_{A^*} and D_A are equal. D_{A^*} is the tracer diffusion coefficient and is related to the self-diffusion coefficient by the correlation factor.

Equations (7) and (8) can be rewritten:

$$J_{A^*} = - D_{A^*} \frac{\partial n_{A^*}}{\partial x} - [L_{A^*A^*} + L_{A^*A}] \frac{(Q_{A^*}^* - \Delta H_F)}{T^2} \frac{dT}{dx} ; \quad (10)$$

$$J_A = + D_A \frac{\partial n_{A^*}}{\partial x} - [L_{AA} + L_{AA^*}] \frac{(Q_A^* - \Delta H_F)}{T^2} \frac{dT}{dx} . \quad (11)$$

It is possible to obtain expressions for D_{A^*} and D_A in terms of the phenomenological coefficients. These relations are given below:

$$D_{A^*} = k \left[\frac{L_{A^*A^*}}{n_{A^*}} - \frac{L_{A^*A}}{n_A} \right] ; \quad (12)$$

$$D_A = k \left[\frac{L_{AA}}{n_A} - \frac{L_{AA^*}}{n_{A^*}} \right] \quad (13)$$

The cross terms L_{AA^*} and L_{A^*A} are equal because of microscopic reversibility, but these terms cannot be neglected with respect to the diagonal terms $L_{A^*A^*}$ and L_{AA} because of correlation effects in the vacancy diffusion process.

Since $n_A \gg n_{A^*}$, $L_{A^*A^*}/n_{A^*} \gg L_{A^*A}/n_A$, thus Eqs. (12) and (13) reduce to

$$D_{A^*} = \frac{k L_{A^*A^*}}{n_{A^*}} = D_{A^*A^*} ; \quad (14)$$

$$D_A = k \left[\frac{L_{AA}}{n_A} - \frac{L_{AA^*}}{n_{A^*}} \right] = D_{AA} - D_{AA^*} \quad (15)$$

But $D_{A^*} = D_A$, therefore

$$D_{A^*} = D_{A^*A^*} = D_{AA} - D_{AA^*} = f D_{AA} \quad (16)$$

D_{AA} is the self-diffusion coefficient and f is the correlation factor. Only the fcc lattice is involved in the present experiment and the correlation factor is 0.78 for this case.^{15/}

Using the above relations it is possible to rewrite the phenomenological expressions in Eqs. (10) and (11):

$$L_{A^*A^*} + L_{A^*A} = \frac{n_{A^*}}{k} D_{A^*A^*} + \frac{n_{A^*}}{k} D_{AA^*} = \frac{n_{A^*}}{k} D_{AA}; \quad (17)$$

$$L_{AA} + L_{AA^*} = \frac{n_A}{k} D_{AA} + \frac{n_{A^*}}{k} D_{AA^*} = \frac{n_A}{k} D_{AA} \quad (18)$$

The last expression is due to the fact that $n_A \gg n_{A^*}$ and $D_{A^*A^*} \approx D_{AA}$. Using these expressions in Eqs. (10) and (11) gives

$$J_{A^*} = -D_{A^*} \frac{\partial n_{A^*}}{\partial x} - \frac{D_{AA} n_{A^*}}{kT^2} (Q_A^* - \Delta H_F) \frac{dT}{dx}; \quad (19)$$

$$J_A = +D_{A^*} \frac{\partial n_{A^*}}{\partial x} - \frac{D_{AA} n_A}{kT^2} (Q_A^* - \Delta H_F) \frac{dT}{dx} \quad (20)$$

It is interesting to note from Eqs. (19) and (20) that the tracer diffusion coefficient enters into the concentration gradient terms whereas the self-diffusion coefficient enters into the temperature gradient terms.

In order to obtain the flux of tracer in the laboratory reference frame, the relative velocity of the two reference frames must be determined. This velocity, V , is given by

$$(n_A + n_{A^*}) V = -(J_{A^*} + J_A) \quad (21)$$

Substituting the lattice flux Eqs. (19) and (20) gives

$$V = \frac{D_{A^*}}{fkT^2} (Q_A^* - \Delta H_F) \frac{dT}{dx} \quad (22)$$

The tracer diffusion coefficient and correlation factor have been substituted for the self-diffusion coefficient. This is the velocity expression that is usually used to measure the quantity $Q_A^* - \Delta H_F$ experimentally using the scratch mark and internal wire technique.

The flux of tracer in the laboratory reference frame is given by

$$J_{A^*}^0 = J_{A^*} + n_{A^*} V \quad (23)$$

Substituting for V and J_{A^*} gives

$$J_{A^*}^0 = -D_{A^*} \frac{\partial n_{A^*}}{\partial x} \quad (24)$$

This equation shows that there is actually no net flux of tracer atoms due to the temperature gradient in the laboratory frame, as required by consideration of momentum conservation.

To obtain the differential equation for the concentration of tracer atoms the continuity equation is used:

$$\frac{\partial n_{A^*}}{\partial t} = - \frac{\partial J_{A^*}^0}{\partial x} = D_{A^*} \frac{\partial^2 n_{A^*}}{\partial x^2} + \frac{D_{A^*} Q_A}{kT^2} \frac{dT}{dx} \frac{\partial n_{A^*}}{\partial x} \quad (25)$$

The activation energy for self-diffusion is given by Q_A . The above parabolic partial differential equation with non-constant coefficients cannot be solved exactly. The non-constant coefficients arise from the fact that both the tracer diffusion coefficient and absolute temperature are functions of position.

The second term on the right-hand side of Eq. (25) causes a shift of the maximum position of the tracer profile toward the cold side; because, in a temperature gradient, the peak of the tracer profile is "eroded" away from the hot side where there is greater diffusion. This erosion would occur even if the velocity, V , of the lattice planes were zero.

An approximate solution to Eq. (25) can be obtained if it is assumed that D_{A^*} and T are constant. This is a reasonable approximation in the region near the lattice marker ($\leq 100\mu$). For a temperature gradient of $300^\circ\text{C}/\text{cm}$ the maximum change in T is 0.3% and the maximum change in D is 6% over this region. For an infinitesimally thin plane source the approximate solution to Eq. (25) is

$$n_{A^*}(x,t) = \frac{n_0}{2[\pi D_{A^*} t + \pi D_w t_w]^{1/2}} \exp \left[- \frac{(x + V_1 t - x_0)^2}{4 D_{A^*} t + 4 D_w t_w} \right] \quad (26)$$

The effective anneal and weld times are t and t_w respectively. D_w is the diffusion coefficient during welding, n_0 is the initial distribution of

tracer, and x_0 is the location of the tracer peak at time $t = 0$. Equation (26) satisfies Eq. (25) if $V_1 = (D_{A^*} Q_A / kT^2) \frac{dT}{dx}$; this can be seen by substituting (26) into (25) and comparing terms. Using the condition $\frac{\partial n_{A^*}}{\partial x} = 0$, the tracer profile maximum is located at the position satisfying $x + V_1 t - x_0 = 0$ at time t . The net shift of the tracer maximum is

$$\Delta x_1 = x(t) - x(0) = x_0 - V_1 t - x_0 = -V_1 t = -\frac{D_{A^*} Q_A}{kT^2} \frac{dT}{dx} t. \quad (27)$$

Far from the interface ($\sim 1\text{mm}$ away) Eq. (26), which represents a shifted gaussian, is not a good approximate solution to Eq. (25). The actual solution to Eq. (25) will be an asymmetric profile, but the peak will still be shifted by the amount given by Eq. (27), since the shifts are small ($\leq 50\mu$) and (27) is an excellent approximation.

Experimentally the initial interface was marked by immobile tracers fixed to the lattice frame of reference, and, since the lattice frame moves with respect to the laboratory frame, Eqs. (22) and (27) must be used together to obtain the shift of the peak of tracer profile with respect to the marker. From Eq. (22) the shift of the laboratory frame with respect to the lattice frame is

$$\Delta x_2 = -\frac{D_{A^*}}{fkT^2} (Q_A^* - \Delta H_F) \frac{dT}{dx} t. \quad (28)$$

Therefore, the shift of the maximum of the tracer profile with respect to the lattice marker is

$$\Delta x = \Delta x_1 + \Delta x_2 = -\frac{D_{A^*}}{kT^2} \left(Q_A + \frac{Q_A^* - \Delta H_F}{f} \right) \frac{dT}{dx} t. \quad (29)$$

The values of the temperature and diffusion coefficient that are used in Eq. (29) are calculated at a plane midway between the tracer profile maximum and the $\text{Hf}^{181}\text{O}_2$ lattice marker. These average values should be used in calculating finite shifts since, in fact, the velocities associated with the shifts are not constant but are also functions of x . Experimentally the diffusion coefficient and temperature are measured at the peak of the tracer profile. The values at this position are only about 0.1% and 2% different from the average values for the temperature and diffusion coefficient respectively.

B. Dilute Substitutional Impurity Thermomigration

Let A represent solvent atoms and B represent impurity tracer atoms. The general expressions for the flux of impurity tracer and solvent atoms in the lattice frame are^{4/}

$$J_A = + D_A \frac{\partial n_B}{\partial x} - [L_{AA}(Q_A^* - \Delta H_F) + L_{AB}(Q_B^* - \Delta H_F)] \frac{1}{T} \frac{dT}{dx}; \quad (30)$$

$$J_B = -D_B \frac{\partial n_B}{\partial x} - [L_{BA}(Q_A^* - \Delta H_F) + L_{BB}(Q_B^* - \Delta H_F)] \frac{1}{T} \frac{dT}{dx} \quad (31)$$

Here Q_A^* and Q_B^* are the heats of transports of solvent atoms and impurity tracer atoms respectively. Since for tracer concentrations the solution is assumed to be ideal, the activity coefficient is independent of concentration, and D_A and D_B can be represented by the following equations:

$$D_A = k \left[\frac{L_{AA}}{n_A} - \frac{L_{AB}}{n_B} \right]; \quad (32)$$

$$D_B = k \left[\frac{L_{BB}}{n_B} - \frac{L_{BA}}{n_A} \right] \quad (33)$$

Since $n_A \gg n_B$, $D_B \approx kL_{BB}/n_B$. D_B is the tracer diffusion coefficient of the dilute impurity. For tracer concentrations, it can also be assumed that the influence of the solute impurity on the self-diffusion of the solvent atoms is negligible. In this case D_A is simply the self-diffusion coefficient of pure solvent atoms; $D_A = kL_{AA}/n_A$. Equations (30) and (31) therefore reduce to

$$J_A = + D_A \frac{\partial n_B}{\partial x} - \frac{n_A D_A}{kT^2} (Q_A^* - \Delta H_F) \frac{dT}{dx} ; \quad (34)$$

$$J_B = - D_B \frac{\partial n_B}{\partial x} - \frac{n_B D_B}{kT^2} (Q_B^* - \Delta H_F) \frac{dT}{dx} \quad (35)$$

The velocity of the lattice frame with respect to the laboratory frame is given by

$$n V = - (J_A + J_B) , \quad (36)$$

where n is the concentration of lattice sites. Substitution of (34) and (35) into (36) gives

$$V = \frac{D_B - D_A}{n} \cdot \frac{\partial n_B}{\partial x} + \frac{1}{nkT^2} [n_A D_A (Q_A^* - \Delta H_F) + n_B D_B (Q_B^* - \Delta H_F)] \frac{dT}{dx} . \quad (37)$$

The first term is the familiar Kirkendall shift and would be important for a non-dilute binary alloy in a temperature gradient; but, under the present circumstances of a dilute alloy, this term is

negligible compared to the second term. Since $n_A \approx n$ and $n_A \gg n_B$, (37) reduces to

$$V = \frac{D_A}{kT} (Q_A^* - \Delta H_F) \frac{dT}{dx} \quad (38)$$

This expression for the drift velocity is, of course, the same as for the pure metal.

The flux of impurity tracer in the laboratory frame is given by

$$J_B^0 = J_B + n_B V \quad (39)$$

Using the equations for J_B and V , J_B^0 becomes

$$J_B^0 = -D_B \frac{\partial n_B}{\partial x} - \frac{n_B}{kT} [D_B(Q_B^* - \Delta H_F) - D_A(Q_A^* - \Delta H_F)] \frac{dT}{dx} \quad (40)$$

Substituting J_B^0 into the continuity equation for n_B gives

$$\frac{\partial n_B}{\partial t} = D_B \frac{\partial^2 n_B}{\partial x^2} + \frac{1}{kT} [D_B(Q_B + Q_B^* - \Delta H_F) - D_A(Q_A^* - \Delta H_F)] \frac{dT}{dx} \frac{\partial n_B}{\partial x} \quad (41)$$

Q_B is the activation energy for the impurity atoms in the solvent matrix. The term proportional to n_B is negligible and has been neglected with respect to the other two terms on the right-hand side of Eq. (41). Again, near the interface ($\leq 100\mu$), the diffusion coefficients and temperature will be approximately constant. The approximate solution to Eq. (41) is then

$$n_B(x, t) = \frac{n_0}{2[\pi D_B t + \pi D_w t_w]^{1/2}} \exp \left[-\frac{(x + V_1 t - x_0)^2}{4D_B t + 4D_w t_w} \right] \quad (42)$$

The shift of the tracer profile maximum with respect to the laboratory marker is

$$\Delta x_1 = -V_1 t = -\frac{1}{kT} [D_B(Q_B + Q_B^* - \Delta H_F) - D_A(Q_A^* - \Delta H_F)] \frac{dT}{dx} t. \quad (43)$$

This equation is seen to be somewhat more complicated than Eq. (27) which represents the shift for tracer self-thermomigration with respect to a laboratory marker.

The shift of the two reference frames for an anneal time t is given by Eq. (38):

$$\Delta x_2 = -\frac{D_A}{kT} (Q_A^* - \Delta H_F) \frac{dT}{dx} t. \quad (44)$$

Therefore, the total shift of the tracer profile maximum with respect to the lattice marker is

$$\Delta x = \Delta x_1 + \Delta x_2 = -\frac{D_B}{kT} (Q_B + Q_B^* - \Delta H_F) \frac{dT}{dx} t. \quad (45)$$

The second term due to the shift of solvent atoms cancels exactly. Here D_B is the tracer diffusion coefficient for the impurity in the solvent matrix A.

Again, average values of the diffusion coefficient and temperature, calculated at a plane midway between the tracer profile maximum and the $\text{Hf}^{181}\text{O}_2$ lattice marker, are used to calculate the effective heat of transport $Q_B + Q_B^* - \Delta H_F$.

III. EXPERIMENTAL PROCEDURE

A. Specimen Preparation

The gold used in this experiment was purchased from Handy and Harmon Corporation in the form of polycrystalline rods 1/4-inch in diameter. The nickel was obtained from Leico Industries, Inc., in the form of polycrystalline rods 2/10-inch in diameter. The gold and nickel were 99.95% and 99.999% pure respectively. The rods were turned to a 3/16-inch diameter on a lathe, cut to the appropriate length, and then threaded at both ends with a 10-32 dye. Each specimen was then spark cut perpendicular to the long axis at two parallel faces separated by 1/8-inch, and the four cut surfaces were then lapped optically flat. A schematic of a typical specimen is shown in Figure 1.

B. Radioactive Isotope Application

A thin uniform layer of radioactive tracer was deposited on each face of the 1/8-inch high disk. A count rate between 50,000 cpm and 150,000 cpm was obtained for all isotope layers. The Au^{195} , Sb^{125} , and Ni^{59} radioactive isotopes were obtained from Nuclear Science and Engineering Corporation. The Hf^{181} isotope was obtained from Oak Ridge National Laboratory. All isotopes were received in approximately 0.5N HCl solutions. The 185-day Au^{195} and 3-year Sb^{125} isotopes were applied by simply drying the solutions onto the optical flats. Both AuCl_3 and SbCl_3 dissociate at temperatures much lower than the welding temperature so that the dissociation was complete in the final welded specimen. Since the specimens were only 0.187 inches in diameter, only a small side cut was permitted. Thus radioactive contamination on the side of the

Figure 1. Schematic of a Specimen.

- ① THREADED END WHICH SCREWS INTO HOT JUNCTION.
- ② WELDED INTERFACES CONTAINING TRACER AND INERT $\text{Hf}^{181}\text{O}_2$ MARKER
- ③ THREADED END WHICH SCREWS INTO COLD JUNCTION

specimen was intolerable. For this reason drying of the radioactive isotope onto the face of the specimen was chosen instead of electroplating since no adequate side mask was found that satisfied the requirement for complete masking without contaminating the plating bath.

The 45-day Hf^{181} was also dried onto the two mating surfaces adjacent to the surfaces deposited with radioactive tracer. The Hf^{181} was in the chemical form HfOCl_2 and was oxidized using concentrated HNO_3 . The resulting non-diffusing radioactive HfO_2 with a very high dissociation temperature served to mark the lattice interface.

The Ni^{59} radioactive isotope with a half-life of 10^5 years and specific activity of approximately 500 $\mu\text{c/gm}$ of nickel had to be electroplated to achieve sufficient activity. The following recipe was used: Seven grams of ammonium sulfate was added to 35 ml of concentrated ammonia; the resulting solution was diluted to 150 ml with distilled water; to 15 ml of the plating solution was added the appropriate amount of radioactive NiCl_2 . In three hours plating time and at a plating temperature of 50°C , approximately 300,000 cpm of Ni^{59} was plated onto the 1/8-inch long middle piece of the specimen. To remove the radioisotope from the side of the cylindrical surface of the specimen, the two parallel faces were painted using red Glyptal paint. The paint was then dried using a sun lamp. The specimen was then etched in concentrated nitric acid for approximately 10 minutes and then rinsed thoroughly in distilled water. The Glyptal was finally removed from the end faces by dissolving in acetone.

C. Welding Apparatus

The next step in the procedure was to reassemble the specimen for welding. A special stainless steel brace was fabricated to support the specimen for mounting in the welding rig. A schematic of the brace is shown in Figure 2. It was possible to line up all three pieces of the specimen with no overlap of edges using this brace. The assembled specimen and brace were then inserted into the molybdenum welding apparatus which is shown in Figure 3. As seen in the figure, the specimen alignment pieces touched the molybdenum body in two adjacent rings with a clearance of approximately 1 mil. This was necessary to keep the alignment pieces from welding to the body of the welding apparatus at the welding temperature. The tightening screws touched the alignment pieces at only one point to keep the alignment pieces straight during welding. After the specimen had been inserted into the welding apparatus the stainless steel brace was removed through one of the three viewing ports. The specimen touched the welding apparatus only at each end, separated by a thin piece of mica to keep the specimen from welding to the alignment pieces. The assembled molybdenum welding apparatus and specimen were then placed in a vertical-tube vacuum furnace. A thermocouple was inserted at a viewing port to monitor the temperature of the specimen. At the welding temperature the specimen was under pressure due to the difference in thermal expansion of the gold and nickel specimens and the molybdenum welding rig. The welding temperature for the gold specimens was approximately 950°C, which is 113°C under the melting point of gold. The effective welding time was on the order of an hour. The nickel specimen was welded at 1200°C for approximately two hours, 250°C below

Figure 2. Stainless Steel Brace for Aligning
Specimen Pieces.

TOP VIEW

SIDE VIEW

Figure 3. Assembled Molybdenum Welding Apparatus
with Specimen.

- ① TIGHTENING SCREWS
- ② APPARATUS BODY
- ③ SPECIMEN ALIGNMENT PIECES
- ④ VIEWING PORT
- ⑤ SPECIMEN

its melting temperature. The radioactive tracer penetration was between 50 and 100 microns during the weld. For the gold runs this amounted to approximately 3% of the total penetration after the temperature gradient anneal for the tracer at the hot interface and approximately 10% for the tracer at the cold interface. During the welding anneal the length of the specimen decreased by approximately 1/2%. This was, of course, expected since uniaxial pressure was required to effect the welds.

All weld attempts were successful. Examination of the welds indicated that they were sound, and this visual observation was corroborated by subsequent lathe sectioning. After the specimen was welded, a small hole approximately 30 mils in diameter and 30 mils deep was drilled into the top of the specimen. The control thermocouple was inserted into this well during the diffusion anneal and actually welded to the specimen.

D. Thermomigration Apparatus

The welded specimen was then placed into the temperature gradient furnace for the diffusion anneal. A schematic of the furnace is shown in Figure 4. During the runs on gold, the specimen was cooled at one end by screwing it into a water-cooled copper base, and it was heated at the other end by screwing it directly into a molybdenum heat conductor. A Pt-Pt, 13%Rh control thermocouple was inserted in a hold along the cylindrical axis of the heat conductor to contact the top of the specimen; this couple controlled the temperature of the specimen at its hottest point. No thermocouples which might possibly adversely affect the temperature gradient by acting as heat sinks were inserted along the specimen length. The specimen was allowed to expand freely upward when heated,

Figure 4. Schematic of Temperature Gradient Furnace.

since only the threaded portion was actually in physical contact with the molybdenum heat conductor. The distance between the welds was measured before and after the diffusion anneal, and no change could be detected using a microscope capable of measuring distances accurate to 0.1 mil.

Before the actual diffusion anneals were performed, the temperature gradient was measured on a dummy copper specimen using a series of four thermocouples along the length of the dummy specimen. Figure 5 is a plot of this temperature distribution. The gradient was found to be linear over the one-inch length of the specimen.

A dynamic vacuum of 10^{-5} mm was maintained within the chamber to reduce conduction and convection losses and also to preserve the life of the molybdenum furnace winding. The heat radiation shield consisted of two concentric tantalum cylinders. An input power of approximately 600 watts was necessary to provide a temperature gradient of nearly $800^{\circ}\text{C}/\text{inch}$ for the gold specimens. About half of this power was necessary to provide the temperature gradient and the remainder to compensate other heat losses. The entire furnace assembly was separated thermally from the water-cooled copper base by ceramic support insulators. This was necessary to keep the input power to a minimum. Even with as much insulation as possible the temperature at the molybdenum furnace winding was estimated to be in excess of 1300°C to maintain a temperature of 1040°C at the top of the gold specimen.

The temperature at the top of the gold specimens was maintained to within $\pm 1^{\circ}\text{C}$ at 1040°C for periods up to two weeks using a Thermac Solid-State Temperature Controller. The control temperature was continuously monitored using a Hewlett-Packard Strip-Chart Recorder. The water

Figure 5. A Typical Temperature Profile Measured Along a
Test Cooper Specimen Using Thermocouples.

temperature at the water reservoir was monitored periodically and found to be within $\pm 1/2^\circ\text{C}$ at approximately 20°C .

A slightly different annealing procedure was required for the nickel specimen. It was not possible to place the nickel specimen directly in contact with the molybdenum heating conductor or the Pt-PtRh thermocouple; because, near its melting point, nickel dissolves platinum and molybdenum, and the resulting alloys melt at approximately 100°C under the melting point of nickel. Thus a non-metallic insert was placed between the nickel specimen and molybdenum heat conductor. The most appropriate material for this purpose was boron nitride which has the desirable properties of being machineable, stable at high temperatures, and having a thermal conductivity near that of nickel. A separate control thermocouple was used for the nickel run, placed about midway between the furnace core and the radiation shield.

E. Sectioning Procedure

During the diffusion anneal the control thermocouple and molybdenum heat conductor welded to the top of the gold specimens. After removal from the furnace, the specimen was cut off at an appropriate distance below the second weld. The molybdenum heat conductor was then mounted in the lathe and the attached specimen was aligned prior to sectioning. Alignment was achieved by bringing the cylindrical axis of the specimen into coincidence with the lathe axis. This was done, using the adjustable chuck, by bringing a line on the cylindrical surface of the specimen, parallel to its cylindrical axis, into parallel alignment with the lathe axis. The readings were taken using a soft-tipped copper pointer as an

electrical contact probe and a Starrett dial guage accurate to 0.1 mil. It was possible to align the cylindrical axis of the specimen to within 0.02 radians of the lathe axis by this method. Both weld planes were lined up perpendicular to the lathe axis by this method. Mechanical support of the 3/16-inch diameter specimens was not necessary since the sandwich welds proved strong enough to withstand the applied cutting tool stresses. The total distances sectioned at the hot and cold interfaces were 2 to 3 mm and 1 mm respectively. Since the average section thickness far from the interface was 12 microns, many sections were required for each interface. Close to the HfO_2 interface approximately 4 micron sections were taken. If smaller sections were attempted, the tool usually rubbed against the surface and poor cuts resulted. The number of sections taken for each interface was usually between 50 and 100. A water-soluble lubricant was used as a cutting aid because the gold chips had a tendency to weld back to the face if the chips were cut dry. The chip plus lubricant were placed on Whatman filter paper and saturated with ethyl alcohol. Most of the lubricant was absorbed by the filter paper; the remainder was burned away using an infrared lamp. This procedure for removing the lubricant was tested on a dummy specimen and found to be completely effective.

F. Weighing and Counting Procedure

The chips were weighed using a Mettler semi-micro balance. The average chip weight was about 8 mg with an error of ± 0.02 mg, giving a percent error between 1/4% and 1/2% in section weights. All radio-activities were assayed using a conventional gamma-ray scintillation

system consisting of a high voltage power supply, amplifier, single channel pulse height analyzer, timer, scaler, and the appropriate scintillation crystal. The Au^{195} , Sb^{125} , and Hf^{181} gammas were counted using a 2-inch diameter by 1/2-inch high thallium activated NaI crystal with an aluminum window. The Au^{195} distribution was determined using a window corresponding to the Au^{195} K X-ray; the Sb^{125} distribution was determined by counting its two highest energy gamma rays, and the Hf^{181} distribution was determined using its highest energy gamma rays. To assay the 6.9 KeV X-ray from Ni^{59} , a 2-inch diameter thallium activated NaI crystal with a 5 mil thick beryllium window was used in conjunction with a low-noise high-gain amplifier. At least 10,000 counts were taken for each chip; this gives a percent error of 1% for the count rate. The specific activity, which is the count rate divided by the chip weight, was thus accurate to approximately 1.1%. To account for radioactive decay and pulse height analyzer window drift during a counting period, the appropriate standard was counted before and after each section. A computer program was written which corrected the specific activity for these factors and printed out the logarithm of the specific activity as a function of distance in microns. The distance parameter was determined by directly adding the chip weights, thereby avoiding error due to tool wear or dial-gauge slippage.

IV. ANALYSIS OF EXPERIMENTAL RESULTS

A. Method Used to Curve Fit a Tracer Profile

In Chapter II the parabolic partial differential equations which describe the tracer distributions for self-thermomigration and tracer impurity substitutional thermomigration in the laboratory reference frame were derived. These equations are written below with n_{A^*} representing the concentration of tracer atoms in the solvent matrix A and n_B representing the concentration of impurity tracer atoms in the solvent matrix A;

$$\frac{\partial n_{A^*}}{\partial t} = D_{A^*} \frac{\partial^2 n_{A^*}}{\partial x^2} + \frac{D_{A^*} Q_A}{kT^2} \frac{dT}{dx} \frac{\partial n_{A^*}}{\partial x}, \quad (25)$$

$$\frac{\partial n_B}{\partial t} = D_B \frac{\partial^2 n_B}{\partial x^2} + \frac{[D_B (Q_B + Q_B^* - \Delta H_F) - D_A (Q_A^* - \Delta H_F)]}{kT^2} \frac{dT}{dx} \frac{\partial n_B}{\partial x}. \quad (41)$$

Since these equations have non-constant coefficients, it is not possible to solve them exactly over the 1 to 3 mm range in x of the tracer spread, inasmuch as the diffusion coefficients and absolute temperature vary considerably over this range.

Therefore, the following method was used for solution: Since the solutions to Eqs. (25) and (41) for constant coefficients are just gaussians in x (the solutions are given by Eqs. (26) and (42)) centered at the extremum positions, a plot of the natural logarithm of the concentration versus x for these solutions is obviously a polynomial in x of order 2. Thus it seemed reasonable to suppose that for a non-zero temperature gradient a plot of the natural logarithm of the experimental tracer concentration could be fit by the method of least squares by a

general polynomial in x of order 2 or higher, depending on the skewness and range of the profile. This method was tried and proved to be very successful. An IBM 7094 computer program was used to fit the experimental log concentrations versus x values with polynomials in x from orders 2 through 8. The best fit curve was chosen on the basis of the minimum standard deviations of the polynomial coefficients and the maximum number of experimental points which fell within one standard deviation. On this basis all curves were best fit with a polynomial of order 3 except in four cases. In three cases, which were order 2 fits, the range of x was between 300 and 400 microns; this verifies experimentally that for a small range of x it is correct to use the constant coefficient solutions to Eqs. (25) and (41). In the other case, which was an order 4 fit, the range of x was about 3300 microns; this order of fit is entirely reasonable since the range was very large. Another interesting point concerning the rejected fits is important. In those cases in which a shift was measured, the rejected fits of orders 3, 4, and 5 gave the same profile maximum to within a few microns. This is excellent proof that the position of the profile maximum given by the least squares fit is independent of the details of the fit.

For the best fit curves the error in the polynomial coefficients was usually between 1% and 2%, and the percentage of experimental points falling within one standard deviation was around 70%. Table I is a summary of the percentage of data points within one standard deviation for all runs.

Table I. A Summary of the Percentage of Data Points

Within One Standard Deviation for All Runs.

Run Number	Radioactive Tracer	Interface	Total Number of Points	Order of Fit	Percentage of Points Within One Std. Dev.
1	Au ¹⁹⁵	cold	56	3	80
1	Au ¹⁹⁵	hot	66	3	74
2	Au ¹⁹⁵	cold	66	3	85
2	Au ¹⁹⁵	hot	98	4	77
3	Au ¹⁹⁵	cold	25	2	70
3	Sb ¹²⁵	cold	46	3	78
3	Au ¹⁹⁵	hot	22	3	68
3	Sb ¹²⁵	hot	63	3	71
4	Ni ⁵⁹	cold	10	2	80
4	Ni ⁵⁹	hot	39	2	67

B. Interface Temperature Measurement and Calculation of Dt Values

It was mentioned in Chapter III that no monitoring thermocouples were placed in contact with a specimen during an anneal because of the possibility of disturbing the linear temperature gradient and the radioactive tracer profile. It might have been possible to approximate the interface temperature by measuring the temperature at each end of the specimen and assuming a linear gradient over the length of the specimen. This method has been used by earlier investigators to determine the temperature at a given point in self-thermomigration experiments. However, it will be shown below that this method of estimating temperature can introduce large errors in the calculated values for the heat of transport.

In all self-thermomigration experiments the measured shifts are proportional to the diffusion coefficients. Most shift expressions are of the form

$$\Delta x = \frac{Dt}{kT^2} \frac{dT}{dx} Q^{**} ; \quad (46)$$

Q^{**} is an effective heat of transport, Δx is the measured shift, and D is the diffusion coefficient. Since the diffusion coefficient $D = D_0 \exp(-Q/kT)$, an error in T is related to an error in D by the relation

$$\frac{\Delta D}{D} = \frac{Q}{kT} \frac{\Delta T}{T} \quad (47)$$

If the interface temperature cannot be measured directly, it is difficult to estimate the temperature by interpolation to better than

$\pm (10 - 20)^\circ\text{C}$ at a diffusion temperature of 1000°K ; the percent error in T is then 1% to 2%. But since Q/kT is of the order of 20, by Eq. (47) this gives an error in D of 20% to 40%. From Eq. (46) this makes Q^{**} uncertain by the uncertainty in D .

A far more precise method for measuring the temperature at the diffusion interface can be used in the present experiment. Using the measured values for the diffusion coefficients determined from the experimental tracer profiles and the known values of D_0 and Q for self-diffusion, the temperatures at the interfaces could be calculated using the equation $D = D_0 \exp(-Q/kT)$. In the present experiment, most diffusion coefficients were accurate to about 5%; thus T could be determined to about 1/4%. It is important to stress that in this experiment the Dt values were determined directly from the experimental data and did not have to be calculated from separate temperature measurements; thus Dt in each case was known within about 5%.

The Dt calculations were made as follows: For an initial instantaneous plane source at $x = x_0$ at $t = 0$ and at a constant temperature T , the natural logarithm of the concentration at time t is given by

$$\log n = \text{const.} - \frac{(x - x_0)^2}{4Dt + 4D_w t_w} = A_0 + A_1 x + A_2 x^2. \quad (48)$$

The only important coefficient is $A_2 = -(4Dt + 4D_w t_w)^{-1}$. The coefficient A_2 is proportional to the second derivative of the log concentration,

$$\frac{\partial^2 \log n}{\partial x^2} = 2A_2 = -2(4Dt + 4D_w t_w)^{-1}. \quad (49)$$

The best fit curves in polynomials of order 3 for the asymmetric gaussians can be represented by the equation

$$\log n = A_0 + A_1 x + A_2 x^2 + A_3 x^3 \quad (50)$$

Therefore,
$$\frac{\partial^2 \log n}{\partial x^2} = 2A_2 + 6A_3 \bar{x} \quad (51)$$

Since the Dt values are calculated at the extremum position, $\bar{x}$ in Eq. (51) is the extremum. Using Eq. (49) as the definition of the slope and also Eq. (51) gives

$$\frac{1}{2} \frac{\partial^2 \log n}{\partial x^2} = -(4Dt + 4D_w t_w)^{-1} = A_2 + 3A_3 \bar{x} \quad (52)$$

Since $A_2 + 3A_3 \bar{x} = -(A_2^2 - 3A_1 A_3)^{1/2}$, Eq. (52) becomes

$$(4Dt + 4D_w t_w)^{-1} = (A_2^2 - 3A_1 A_3)^{1/2} \quad (53)$$

Equation (53) was used to calculate the Dt values at the tracer peak using the best fit values A_1, A_2, A_3 , and the welding correction $D_w t_w$. Table II gives the best fit polynomial coefficients for Runs 1 and 2 for Au¹⁹⁵ self-thermomigration and Run 4 for Ni⁵⁹ self-thermomigration. Table III gives the best fit polynomial coefficients for Run 3 for Sb¹²⁵ dilute impurity thermomigration in gold. The tracer diffusion coefficient of Au¹⁹⁵ in gold has been measured by Gilder^{16/} who obtained $D_0 = 0.107 \text{ cm}^2 \text{ sec}^{-1}$ and $Q = 1.83 \text{ eV}$. The tracer diffusion coefficient of Ni⁶³ in nickel has been measured by MacEwan et al.^{17/} who obtained

Table II. Summary of the Polynomial Coefficients for the Best Fit Curve in X^n of the Logarithm of Specific Activity of Au^{195} in Gold for Runs 1 and 2 and Ni^{59} in Nickel for Run 4.

Run No.	Interface	Order of Fit	A_0	$A_1(10^2 \text{ cm}^{-1})$	$A_2(10^3 \text{ cm}^{-2})$	$A_3(10^3 \text{ cm}^{-3})$	$A_4(10^3 \text{ cm}^{-4})$
1	cold	3	6.026 ± 0.031	3.456 ± 0.030	-5.044 ± 0.080	13.94 ± 0.63	
1	hot	3	6.869 ± 0.015	1.381 ± 0.007	-1.049 ± 0.008	1.645 ± 0.030	
2	cold	3	5.778 ± 0.031	2.815 ± 0.017	-2.566 ± 0.026	4.190 ± 0.120	
2	hot	4	5.765 ± 0.015	1.445 ± 0.006	-0.8372 ± 0.0079	1.628 ± 0.038	-1.300 ± 0.062
4	cold	2	8.079 ± 0.141	8.215 ± 0.203	-27.36 ± 0.64		
4	hot	2	8.152 ± 0.075	5.304 ± 0.065	-11.38 ± 0.13		

Table III. Summary of Polynomial Coefficients for the Best Fit Curve of the Logarithm of Specific Activity of Au¹⁹⁵ and Sb¹²⁵ in Gold for Run 3.

Radioactive Tracer	Interface	Order of Fit	A ₀	A ₁ (10 ² cm ⁻¹)	A ₂ (10 ³ cm ⁻²)	A ₃ (10 ³ cm ⁻³)
Au ¹⁹⁵	cold	2	-54.72 ± 0.83	22.12 ± 0.27	-17.70 ± 0.21	
Sb ¹²⁵	cold	3	6.165 ± 0.034	1.674 ± 0.019	-1.661 ± 0.031	3.393 ± 0.150
Au ¹⁹⁵	hot	3	-73.60 ± 1.50	18.24 ± 0.38	-12.02 ± 0.32	23.87 ± 0.87
Sb ¹²⁵	hot	3	6.018 ± 0.022	0.9008 ± 0.0063	-0.4875 ± 0.0050	0.6558 ± 0.0112

$D_0 = 3.36 \text{ cm}^2 \text{ sec}^{-1}$ and $Q = 3.03 \text{ eV}$. These measurements were used to calculate the temperature at the profile maximum.

The temperature gradient was calculated by using the calculated values of temperature at the hot and cold interfaces of a given specimen and the measured distance between them. The temperature gradients were thus accurate to about 4%. The only purpose of the cold interface was to measure the temperature at another point along the specimen so that an accurate determination of the temperature gradient could be made.

C. Shift of Gold Tracer

Two tracer self-thermomigration runs were performed in gold using Au^{195} . Figures 6 and 7 are plots of the Au^{195} distributions at the cold and hot interfaces in Run 1. A shift of $-16 \pm 3\mu$ was measured at the hot interface. The largest source of error in the shift measurement is the location of the $\text{Hf}^{181}\text{O}_2$ layer. This was done to within about $\pm 2\mu$ by taking very small cuts through the interface. Figure 8 is a plot of the Au^{195} penetration profiles versus distance from the profile maximum squared in Run 1. The skewness of the profiles due to the temperature gradient is clearly evident from this figure. The average of the high and low temperature branches was obtained by reflecting the low temperature wing of a given profile about the extremum to the high temperature side and averaging with the high temperature branch; the slope of the plot of the average of the two branches versus $(x - \bar{x})^2$ also gives the Dt values at the tracer peak.

Figures 9 and 10 are plots of the Au^{195} distributions at the cold and hot interfaces in Run 2. The range of x is larger than for Run 1.

Figure 6. Distribution of Au¹⁹⁵ Tracer at the Cold Interface in Run 1.

Figure 7. Distribution of Au^{195} Tracer and $\text{Hf}^{181}\text{O}_2$ Marker
at the Hot Interface in Run 1.

Figure 8. Au^{195} Penetration Profiles at the Hot and Cold
Interfaces in Run 1.

Figure 9. Distribution of Au¹⁹⁵ Tracer at the Cold Interface
in Run 2.

Figure 10. Distribution of Au^{195} Tracer and $\text{Hf}^{181}\text{O}_2$ Marker
at the Hot Interface in Run 2.

A shift of $-35 \pm 3\mu$ was measured at the hot interface. Figure 11 is a plot of the Au^{195} penetration profiles versus distance from extremum squared in Run 2.

D. Shift of Antimony Tracer

The diffusion coefficient of Sb^{125} has not been previously measured in gold. Thus it was necessary to diffuse both Au^{195} and Sb^{125} together in gold to establish an accurate temperature scale. The Sb^{125} Dt values were determined from the antimony tracer profiles. The temperature at the antimony profiles was determined from the gold Dt values and the known diffusion coefficient of Au^{195} in gold. Figures 12 and 13 show the Sb^{125} and Au^{195} tracer distributions at the cold and hot interfaces respectively. An Sb^{125} tracer profile shift of $+51 \pm 3\mu$ was measured at the hot interface. In this run it was actually possible to separate the hot interface with the lathe cutting tool at a distance of a few microns away. This was probably possible because the diffusion time for this run was 1 day whereas the diffusion time for Runs 1 and 2 was about 10 days, all at about the same temperature; welding was therefore probably less complete. Figures 14 and 15 are plots of Au^{195} and Sb^{125} penetration profiles versus distance from the extremum squared respectively in Run 3.

E. Shift of Nickel Tracer

Figure 16 is a plot of the Ni^{59} distribution at the cold interface in Run 4. In this run the hot interface was sectioned first and no appreciable shift was determined. Thus, large 1 mil cuts were taken through the cold interface since only the temperature was wanted at that point. Figure 17 is a plot of the Ni^{59} distribution at the hot interface

Figure 11. Au^{195} Penetration Profiles at the Hot and Cold Interfaces in Run 2.

Figure 12. Distribution of Sb^{125} and Au^{195} Tracers
at the Cold Interface in Run 3.

Figure 13. Distribution of Sb^{125} and Au^{195} Tracers
at the Hot Interface in Run 3.

Figure 14. Au^{195} Penetration Profiles at the Hot and Cold Interfaces in Run 3.

Figure 15. Sb^{125} Penetration Profiles at the Hot and Cold Interfaces in Run 3.

Figure 16. Distribution of Ni⁵⁹ Tracer at the
Cold Interface in Run 4.

Figure 17. Distribution of Ni^{59} Tracer and $\text{Hf}^{181}\text{O}_2$ Marker
at the Hot Interface in Run 4.

in Run 4. It was necessary to make a mass absorption correction since various size cuts were taken at this interface. Ni^{59} decays to Co^{59} by emitting a 6.9 KeV X-ray and the mass absorption correction in nickel is appreciable. Nevertheless, the calculated position of the profile maximum was not changed by correcting the specific activities for mass absorption.

The temperature at a point in contact with the boron nitride near the top of the nickel specimen was maintained at approximately 1550°C. The temperature at the hot interface was thus estimated to be approximately 1200°C. The actual measured value was only 1066°C. Thus a much smaller amount of diffusion occurred than was expected, resulting in a shift measurement which fell within the experimental uncertainty.

The boron nitride insert which was between the molybdenum heat conductor and the nickel specimen, for reasons explained earlier, is probably the reason for the lower temperature at the hot interface. Finite temperature drops probably occurred at both boron nitride-metal interfaces because after the run it was evident that the threaded nickel specimen had made poor thermal contact with the brittle boron nitride, and the threads had actually melted away near the top of the specimen during the run. Apparently, initially a fair thermal contact was achieved but was lost near the nickel melting point because of the inability of the metal and ceramic to fuse. This problem was not encountered in the gold runs because the threaded gold specimens could be screwed directly into the molybdenum, with the result that at the beginning of the run the specimen and molybdenum heat conductor fused, maintaining good thermal contact.

Due to these experimental difficulties the tracer spread at both the hot and cold interfaces was less than 500μ . A polynomial in x of order 2, as expected, gave the best fit curves for both interfaces. A shift of $-0.8 \pm 2\mu$ was obtained at the hot interface. Figure 18 is a plot of the Ni^{59} penetration profiles versus distance from extremum squared in Run 4.

Figure 18. Ni^{59} Penetration Profiles at the Hot and Cold Interfaces in Run 4.

V. DISCUSSION OF RESULTS

A. Comparison of Self-Thermomigration Results with Theory

Table IV includes all the measured and calculated parameters for Runs 1 and 2 for tracer self-thermomigration in gold. Equation (29) was used to calculate the effective heat of transport $Q_{Au} + (Q_{Au}^* - \Delta H_F)/f$ of the gold atoms. The temperature gradients for the two runs agree almost exactly within experimental error, indicating that the specimens were annealed under nearly identical conditions. The major difference in the effective heats of transport is attributable to errors in locating the $Hf^{181}O_2$ layer. The average value of the effective heat of transport $Q_{Au} + (Q_{Au}^* - \Delta H_F)/f$ is 1.60 ± 0.27 eV. Using $Q_{Au} = 1.83$ eV for the activation energy of Au^{195} in gold,^{16/} $\Delta H_F = 0.98$ eV for the gold vacancy formation energy,^{18/} and $f = 0.78$ for the fcc lattice^{15/} gives a value for the heat of transport of $Q_{Au}^* = 0.80 \pm 0.27$ eV.

The motion energy of gold atoms^{18/} has been measured to be $\Delta H_M = 0.82 \pm 0.05$ eV. Comparing the measured value of the heat of transport with the motion energy indicates excellent agreement with Huntington's theory for single band metals. Apparently, as predicted, the contribution to the heat of transport from the static temperature gradient far outweighs the contributions from the thermoelectric field and charge carrier-ion interaction. Thus, the diffusing atom carries almost all of its migration energy with it when jumping from a given site to an adjacent vacant site.

The presently measured value of $Q_{Au}^* = 0.80$ eV can be compared with the three previous measurements in which scratch marks and internal wires

Table IV. Parameters Describing the Thermomigration of Au¹⁹⁵ in Gold for Runs 1 and 2.

Run No.	Interface	Time (10 ⁵ sec)	Diff. Coeff. (10 ⁻¹⁰ cm ² sec ⁻¹)	Temp. (°C)	Temp. Grad. (°C cm ⁻¹)	Shift (μ)	$Q + \frac{Q^* - \Delta H_F}{f}$ (eV)
1	cold	7.52	0.854 ± 0.005	741 ± 3			
1	hot	7.52	4.98 ± 0.13	834 ± 2	315 ± 12	-16 ± 3	1.43 ± 0.27
2	cold	8.50	1.56 ± 0.05	771 ± 2			
2	hot	8.50	8.47 ± 0.44	867 ± 3	309 ± 12	-35 ± 3	1.76 ± 0.18

were used. Adda et al.^{7/} obtained $Q_{Au}^* = \Delta H_F = 0.98$ eV using the internal wire technique; Meechan and Lehman^{6/} using the internal wire technique obtained $Q_{Au}^* = 0.78$ eV for one run, and larger values for their other two runs; and Jaffe and Shewmon^{5/} obtained $Q_{Au}^* = 0.61$ eV using the scratch mark technique. The present result of $Q_{Au}^* = 0.80$ eV agrees almost exactly with the first result obtained by Meechan and Lehman. It is possible that the null result observed by Adda et al. was due to improper bonding between the specimen and inclusion wire, the net effect being that the wire does not move with the velocity of the lattice. It should be pointed out that self-thermomigration experiments are difficult to carry out accurately, regardless of which method is used, because the thermomigration effect is so small.

Table V includes all the measured and calculated parameters for Run 4 for tracer self-thermomigration in nickel. The calculated value of the effective heat of transport $Q_{Ni} + (Q_{Ni}^* - \Delta H_F)/f$ is 2.9 ± 7.2 eV. The large experimental error is due to the fact that an extremely small shift was obtained because the temperature at the hot interface was far lower than expected. Using $Q_{Ni} = 3.03$ eV for the activation energy of Ni⁵⁹ in nickel,^{17/} and $f = 0.78$ for the fcc lattice^{15/} gives $Q_{Ni}^* - \Delta H_F = -0.10$ eV. Using a value for the nickel formation energy of 1.4 eV,^{19/} one derives a value of $Q_{Ni}^* = 1.3 \pm 7.2$ eV for the nickel self-thermomigration heat of transport. Because of this very large experimental error no definite conclusions concerning the effect of the charge carrier-ion interaction can be made. Klemens and Weaver^{20/} obtained a negative sign for $Q_{Ni}^* - \Delta H_F$; this agrees with the above value of -0.10 eV for this quantity.

Table V. Parameters Describing the Thermomigration of Ni^{59} in Nickel for Run 4.

Interface	Time (10^6 sec)	Diff. Coeff. ($10^{-11} \text{ cm}^2 \text{ sec}^{-1}$)	Temp. ($^{\circ}\text{C}$)	Temp. Grad. ($^{\circ}\text{C cm}^{-1}$)	Shift (μ)	$Q + \frac{Q^* - \Delta H_F}{f}$ (eV)
cold	1.32	0.430 ± 0.01	1008 ± 2			
hot	1.32	1.40 ± 0.02	1066 ± 2	185 ± 9	-0.8 ± 2	2.9 ± 7.2

B. Comparison of the Antimony Impurity Thermomigration Result with Theory

Table VI includes all the measured and calculated parameters for Run 3 for Sb^{125} impurity thermomigration in gold. Equation (45) was used to calculate the effective heat of transport $Q_{\text{Sb}} + Q_{\text{Sb}}^* - \Delta H_{\text{F}}$ of the impurity antimony atoms. This value is $Q_{\text{Sb}} + Q_{\text{Sb}}^* - \Delta H_{\text{F}} = -1.61 \pm 0.16$ eV. Q_{Sb} is the antimony activation energy in gold. It was possible to measure Q_{Sb} directly in this experiment because D values of Sb^{125} in gold were measured at two positions in the rod and the temperature at these positions was measured using Au^{195} tracer. Q_{Sb} was measured to be 1.39 ± 0.17 eV. Gilder^{16/} estimated a value of 1.2 eV for this parameter on the basis of two points while studying electromigration of Sb^{125} in gold. A value of $Q_{\text{Sb}} = 1.39$ eV compares favorably with the measured activation energy for diffusion of antimony in silver^{21/} which is 1.67 eV. Using $Q_{\text{Sb}} = 1.39$ eV and $\Delta H_{\text{F}} = 0.98$ eV (the vacancy formation energy adjacent to a solute atom is assumed to be equal to the formation energy in the pure metal) gives $Q_{\text{Sb}}^* = -2.02 \pm 0.23$ eV. This is a very large negative heat of transport. It indicates that there is a net flux of antimony atoms up the temperature gradient in gold. Biermann et al.^{22/} have investigated the heat of transport of antimony in silver by measuring the thermal gradient redistribution of antimony in silver under steady state conditions. In the present notation, their measured value for antimony in silver is $Q_{\text{Sb}}^* - \Delta H_{\text{F}} = -1.47 \pm 0.27$ eV. This value can be compared with the present calculated value for antimony in gold; $Q_{\text{Sb}}^* - \Delta H_{\text{F}} = -3.00 \pm 0.23$ eV. The values compare favorably and indicate that basically the same interactions are taking place in both gold and silver.

Table VI. Parameters Describing the Thermomigration of Sb^{125} in Gold for Run 3.

Radioactive Tracer	Interface	Time (10^4 sec)	Diff. Coeff. ($10^{-10} \text{ cm}^2 \text{ sec}^{-1}$)	Temp. ($^{\circ}\text{C}$)	Temp. Grad. ($^{\circ}\text{C. cm}^{-1}$)	Shift (μ)	$Q + Q^* - \Delta H_F$ (eV)
Au^{195}	cold	9.80	0.797 ± 0.073	738 ± 4			
Sb^{125}	cold	9.80	20.9 ± 2.1				
Au^{195}	hot	9.80	6.20 ± 0.12	848 ± 2			
Sb^{125}	hot	9.80	100.9 ± 7.3		347 ± 14	51 ± 3	-1.61 ± 0.16

The present result indicates, according to Huntington's theory, that the electron-impurity ion interaction is very large (as might be expected, since the valence difference between antimony and gold is +4) and drives the antimony atoms to the hot end of the specimen. This means that the cold electrons moving up the temperature gradient deliver more momentum to the impurity atoms than the hot electrons moving down the temperature gradient. This can only be possible if the scattering cross section of the impurity by the electrons is a decreasing function of energy.

Gerl^{9/} has investigated theoretically the effect of the temperature gradient on impurity atoms in great detail. His expression for the force acting on an impurity atom (which is proportional to the negative of the heat of transport contribution of the heat carrier-impurity ion interaction) is

$$\frac{F_z}{\nabla T} = -M A_z(E_F) \left[1 + 2 \left(\frac{dA/A}{dE/E} \right) \right]_{E_F} \quad (54)$$

M is a characteristic of the matrix, $A_z(E_F)$ is the scattering cross section of the impurity ion, evaluated at the Fermi energy, and $\left(\frac{dA/A}{dE/E} \right)_{E_F}$ represents the change in the scattering cross section with electron energy evaluated at the Fermi energy. The present experimental result would indicate that the second term on the right in Eq. (54) is negative and less than one. Gerl also derived a more complicated expression for Eq. (54), taking into account the scattering effect of the neighboring vacancy of the impurity atom. Using known thermoelectric power data, the contribution to the heat of transport due to the electron-antimony ion

interaction in silver at 900°C was calculated to be $Q^* = -0.5$ eV. A similar calculation was not made for antimony in gold, but the theoretical result in silver does indicate that there could be a large negative heat of transport contribution in gold due to the electron-impurity ion interaction in agreement with the present result.

Apart from atomistic arguments, a negative value for Q_{Sb}^* might be expected on purely classical grounds, since the increasing solubility of the impurity with increasing temperature furnishes a thermodynamic driving force tending to move the impurities up the temperature gradient.

VI. SUMMARY AND CONCLUSIONS

The effect of large thermal gradients on the mass transport of Au^{195} and Sb^{125} in gold and Ni^{59} in nickel has been investigated. Specimens in the form of rods containing two welded interfaces separated by 1/8-inch were fabricated. Each interface contained a layer of the appropriate tracer and an inert radioactive $\text{Hf}^{181}\text{O}_2$ marker. The specimens were annealed in a vacuum furnace which provided a temperature gradient of approximately $300^\circ\text{C}/\text{cm}$. The radioactive penetration profiles at the hot and cold interfaces were determined experimentally by sectioning the specimen on a lathe and assaying the radioactivity in each section. The penetration profiles, which were skewed gaussians, were curve fit by the method of least squares. The temperature at each interface and the temperature gradient were determined from the measured D values and the known tracer self-diffusion coefficient.

During the temperature gradient anneal the maximum of the tracer profile at the hot interface shifted with respect to the $\text{Hf}^{181}\text{O}_2$ marker. Using the measured shift values, the heat of transport of Au^{195} in gold was measured to be $Q_{\text{Au}}^* = 0.80 \pm 0.27$ eV. This value supports Huntington's theory of thermomigration of solvent atoms in single band metals. The theory predicts that the static temperature gradient contribution to the heat of transport is approximately equal to the atomic migration energy and is two orders of magnitude larger than the thermoelectric field and charge carrier-ion interaction effects.

The heat of transport of Ni^{59} in nickel was estimated to be $Q_{\text{Ni}}^* = 1.3 \pm 7.2$ eV. Because the measured value for the shift was within

the experimental error, a large uncertainty in Q_{Ni}^* resulted. It is therefore not possible to draw conclusions concerning the magnitude of the charge carrier-ion interaction.

The experimentally determined value of the Sb^{125} heat of transport in gold was found to be $Q_{Sb}^* = -2.02 \pm 0.23$ eV. According to Gerl's theory for dilute impurity thermomigration, this large negative number indicates that the charge carrier-impurity ion interaction is the dominant driving force for Sb^{125} impurity thermomigration in gold, because the cold electrons moving up the temperature gradient impart more momentum to the impurity atom than the hot electrons moving down the temperature gradient. Q_{Sb}^* compares favorably with the theoretically calculated value for the heat carrier-impurity ion interaction of $Q^* = -0.5$ eV for antimony thermomigration in silver.

BIBLIOGRAPHY

1. C. Ludwig, Sitzungsber Akad. Wiss. Wien, Math. Naturw. Kl. 20, 539 (1856).
2. Ch. Soret, Arch. de Genev 3, 48 (1879).
3. S. R. de Groot, "Thermodynamics of Irreversible Processes," Interscience Publishers, New York (1951).
4. Y. Adda and J. Philibert, "La Diffusion dans les Solides," Institut National des Sciences et Techniques Nucleaires, Saclay (1966).
5. D. Jaffe and P. G. Shewmon, Acta Met. 12, 515 (1964).
6. C. J. Meechan and G. W. Lehman, J. Appl. Phys. 33, 634 (1962).
7. Y. Adda, G. Brebec, N. V. Doan, M. Gerl, and J. Philibert, Symp. Thermodynamique Mat. Nucl. AIEA SM 66/55, Vienna (1965).
8. H. B. Huntington, RPI Report 1066-14 (1968).
9. M. Gerl, J. Phys. Chem. Solids 28, 725 (1967).
10. R. A. Oriani, U.S. Steel Corp. Report No. 1406 (1968).
11. V. B. Fiks, Soviet Physics - Solid State 5, 2549 (1964).
12. K. Wirtz, Z. Phys. 44, 221 (1943).
13. J. A. Brinkman, Phys. Rev. 93, 345 (1954).
14. D. Lazarus, in "Energetics in Metallurgical Phenomena," Gordon and Breach, New York (1965).
15. K. Compaan and Y. Haven, Trans. Farad. Soc. 54, 1498 (1958).
16. H. M. Gilder, Thesis, University of Illinois (1965).
17. J. R. MacEwan, J. U. MacEwan, and L. Yaffe, Canad. J. Chem. 37, 1623 (1959).
18. R. O. Simmons, J. S. Koehler, and R. W. Bulluffi, Radiation Damage in Solids 1, 155 (1962).
19. T. Nakamura, J. Phys. Soc. Japan 16, 2167 (1961).
20. D. Klemens and H. Wever, unpublished work.
21. E. Sonder, L. Slifkin, and C. T. Tomizuka, Phys. Rev. 93, 970 (1954).
22. W. Biermann, D. Heitkamp, and T. S. Lundy, Acta Met. 13, 71 (1965).

VITA

Willis Mock, Jr. was born December 23, 1938 at Thomasville, North Carolina. In 1948 his family moved to Greensboro, North Carolina. He was graduated from Greensboro Senior High School in June, 1957. In May, 1961, he received the B.S. degree in Physics from North Carolina State University. He began graduate study at the University of Florida in September, 1961, and received the M.S. degree in Physics in April, 1963.

He entered the Graduate College of the University of Illinois in September, 1963. He held both teaching and research assistantships during his graduate study.

He is a member of the American Association of Physics Teachers.