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VACANCY CONCENTRATION AND PRECIPITATION
IN QUENCHED PURE GOLD AND GOLD-SILVER
ALLOYS.

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VACANCY CONCENTRATION AND PRECIPITATION
IN QUENCHED PURE GOLD AND GOLD-SILVER ALLOYS
DISSERTATION

Presented in Partial Fulfillment of the Requirements
for the Degree Doctor of Philosophy in the
Graduate School of The Ohio State University

By

Frederick John Fraikor, B. S.

* * * * *

The Ohio State University

1965

Approved by

Adviser

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DEDICATION

This work is dedicated to
my wife, Arlene.

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The author wishes to acknowledge the advice and encouragement of Professor John Hirth and Professor Gordon Powell.

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	iii
VITA	iv
LIST OF TABLES	vi
LIST OF ILLUSTRATIONS	vii
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	8
RESULTS AND DISCUSSION	31
Gold	
Alloys	
Speciment Size Effect	
Interaction of Dislocations with Vacancy	
Precipitates	
Etch Pits and Surface Contamination of Foils	
CONCLUSIONS	177
REFERENCES	182

LIST OF TABLES

Table	Page
1. Analysis of Impurities in Au and Ag	16
2. Analysis of Ultra Pure Argon	20
3. Vacancy Concentration Deduced from Dilatometer Measurements	41 a
4. Vacancy Concentration Deduced from Precipitate Density	70 a
5. Properties of Vacancies in Au and Ag	118 a

LIST OF ILLUSTRATIONS

Figure	Page
1. Single Crystal Growing Furnace	11
2. Control Board for Crystal Furnace	13
3. Graphite Mold	15
4. Au-Ag Binary Phase Diagram	19
5. Cross-section of Dilatometer	23
6. Schematic View of Dilatometer	25
7. Electropolishing Unit	30
8. Dilatometer Annealing Curve for Gold Wires Heated in Dry Argon	36
9. Annealing Curve for Gold Wire in Commercial Argon	37
10. Au Single Crystal Annealing Curve	38
11. Volume Change Versus Reciprocal of Quench Temperature for Gold	40
12. Vacancy Concentration Versus Reciprocal of Quench Temperature	44
13. Volume Change Versus Dilatometer Specimen Diameter	44
14. Black Spot Vacancy Precipitates in Pure Gold	49
15. Transmission Photograph of Gold Quenched from 1000°C and Aged at 20°C and 100°C	52
16. Tetrahedra in Gold Quenched from 1025°C and Aged at 100°C	55

Figure		Page
17.	Precipitate Denuded Zone in Quenched Gold	57
18.	Low Magnification Photomicrograph of Tetrahedra in Quenched Gold	61
19.	Pure Gold Quenched from 600°C and Annealed at 100°C	63
20.	Black Spot Tetrahedra in Gold Quenched from 600°C	65
21.	Silcox-Hirsch Mechanism of Stacking- fault Tetrahedra Formation	68
22.	Tetrahedra in Gold Quenched from Commercial Argon Atmosphere	77
23.	Grain Boundary Denuded Zone in Gold	79
24.	Dilatometer Annealing Curve for 80%Au Alloy Wires	90
25.	Annealing Curve for 80%Au Wires Quenched Below 900°C	91
26.	Curve for 80%Au Single Crystals	92
27.	Curve for 80%Au Crystals Quenched below 900°C	93
28.	Curve for 60%Au Alloy Wires	94
29.	Curve for 60%Au Single Crystals	95
30.	Curve for 20%Au Alloy Wire	96
31.	Volume Change Versus Reciprocal of Quench Temperature for Au-Ag Alloy Dilatometer Specimens	98
32.	Defect Structure of 80%Au Alloy Foil Quenched from 1000°C	101
33.	80%Au Quenched from 1000°C and Annealed at 100°C	103

Figure		Page
34.	80%Au Quenched from 1000°C	105
35.	Denuded Zone in 80%Au	107
36.	Microcrack in Quenched 80%Au Foil	109
37.	60%Au Foil Quenched from 1000°C	111
38.	Pure Ag Foil Quenched from 900°C	114
39.	80%Au Foil Quenched from 600°C	124
40.	80%Au Foil Quenched from 600°C at Higher Magnification	126
41.	80%Au Foil Quenched from 1000°C and Annealed at 20°C	128
42a.	Dislocation Interaction with Vacancy Precipitates in Quenched Gold	142
42b.	Sequence of Dislocation Moving Around Vacancy Precipitates	144
43.	Row of Tetrahedra in Quenched Gold	149
44a.	Glissile Loops in 80%Au Foil	154
44b.	Higher Magnification View of 80%Au Foil	156
45.	Bow-out of Dislocation in 60%Au	159
46.	Dislocations in Quenched 60%Au	161
47.	Dislocation Interaction in 60%Au	163
48.	Hexagonal Loops of Surface Contamination	167
49.	Lamellar Structure of Surface Contamination on 80%Au Foil	169

50.	Crystallographic Voids Produced in 80% Quenched Gold	171
51.	Voids in 100%Au Quenched from 600°C	173
52.	Voids in Gold Quenched from 1025°C	175

INTRODUCTION

Historically, the concept of vacant sites in a solid was first noted by the Roman writer Titus Lucretius Carus (c. 98 - 55 B.C.). In his discourse, "On the Nature of Things," Lucretius advanced the argument that "things which look to us hard and dense must consist of particles more hooked together, and be held in union, being welded all through with branch-like elements."¹ He further recognized that "all things are not on all sides jammed together and kept in by body: there is also void in things." Although, of course, Lucretius was not aware of actual vacant lattice sites as we recognize them today, he was cognizant of the fact that voids, porosity, density, etc., did contribute significantly to the observed properties of the material. Similarly, in recent years, a growing awareness of the significant role of lattice imperfections on material properties has stimulated a vast amount of research on the exact nature of vacancies and vacancy complexes.

The first early scientific work on vacancies was pioneered by such physicists as Frenkel, Schottky, Wagner and others who investigated point defects in thermal equilibrium in ionic crystal lattices.^{2,3} These authors pointed out that point defects are thermodynamically stable in appreciable concentrations in a crystal lattice.

The equilibrium number of vacancies rises rapidly with increasing temperature, and for most common metals has a value of about 10^{-4} near the melting point. Since this corresponds to one vacant lattice site for every 10,000 occupied sites, it was quickly realized that a large number of vacancies must migrate to positions in the lattice where they can be annihilated to maintain equilibrium if the temperature is suddenly lowered. This question was posed by Seitz and Huntington,⁴ Nabarro⁵ and Frank⁶ who postulated that these excess vacancies could condense on lattice planes to form dislocation loops.

Even earlier, however, a number of investigators became interested in the role of vacancies in the area of diffusion in metals. One of the prevailing theories at that time (1940's) for the mechanism of self-diffusion in most metals was a direct interchange of adjacent atoms. However, Kirkendall noted a net transport of mass in the brass-copper system,⁷ a phenomenon which could not occur by a simple exchange mechanism. Da Silva and Mehl⁸ subsequently confirmed the fact that the marker movement in the diffusion couples was indeed due to a flow of vacancies. A mathematical analysis of the Kirkendall effect was also provided by Darken.⁹

If the flow of atoms of component A is greater than the opposite flow of B atoms, then the net movement of vacancies will be toward the

side of component A. However, Seith¹⁰ has noted a "retrograde" movement of markers in the direction of the fastest moving component due to a vacancy concentration gradient. This observation further stimulated questions about the effect of vacancies and their movement during metal diffusion.

Most of the treatments thus far of mass flow assume that the cross-sectional area of the diffusion couple remains constant during diffusion. Furthermore, it is assumed that the diffusion of A atoms is greater than that of the B atoms over the entire concentration range with vacancies in local equilibrium throughout the diffusion zone.

Unfortunately, these assumptions are apparently invalid in many instances. Ruth^{11, 12} has noted that in diffusion couples of Au-Ag, a large amount of porosity is produced on the side of the more rapidly moving silver component. Similar pores are also associated with a lateral contraction of the couple on the side of the more rapidly diffusing component and a slight bulging on the other side of the interface. The porosity is apparently caused by the condensation of vacancies; the porosity zone itself moves as diffusion proceeds, thus always occurring at a particular composition.¹³

It is apparent, then, that the formation of these voids and protrusions produces a cross-sectional area change and that the equilibrium of vacancies is probably not maintained by the simple elimination of

vacancies at sinks as was previously assumed by Darken, Mehl, and others. The question then arises as to the origin of these excess vacancy clusters and of their behavior prior to, and after diffusion has taken place.

Recent work along these lines by Zuilichem and Burgers¹⁴ shows that while the condensation of quenched-in vacancies in a 95 at. % Au - 5 at. % Pt alloy gave rise to tetrahedral arrangements of stacking faults, diffusion in a Au-Pt-Au couple produced true pores on the gold side. The authors concluded that vacancy condensation in this alloy could give rise both to the formation of stacking faults and to the formation of pores. They further posed the question as to whether stacking fault effects may precede pore formation in diffusion.

In an attempt to answer some of these recent questions, a great deal of current research has been focused on the behavior of lattice defects prior to and during diffusion in metals. Although some excellent vacancy concentration measurements have been made by Simmons and Balluffi¹⁵ by lattice X-ray measurements while at elevated temperatures, the majority of experimental methods utilize specimens quenched from elevated temperatures to retain the vacancies. A good summary of the various experimental techniques and appraisals of the present situation regarding lattice defects in quenched metals have been presented by Van Bueren,¹³ Damask and Dienes,¹⁶ Amelinckx,¹⁷ and more recently, at the International Conference held at Argonne in 1964.¹⁸

Although any physical property that depends sensitively and proportionally on the concentration of defects may be used to measure vacancy concentration, one of the first methods used was electrical resistivity.¹⁹ The general procedure is first to quench the specimen rapidly from an elevated temperature to preserve the equilibrium concentration of vacancies. The quenched samples are subsequently annealed and observations are made of the resistivity change as a function of time. The concentration is proportional to ρ so that

$$\rho = Ae^{-E_f/kT_Q}$$

where A is the pre-exponential factor which includes entropy, geometrical factors and the contribution to resistivity per unit atomic concentration of vacancies. The value of the energy of formation, E_f , can be obtained by measuring the resistivity change from various quench temperatures.

The migration energy, E_m , is experimentally derived by studying the resistivity decay kinetics at various annealing temperatures. Resistivity measurements of this type have been made for gold,²⁰⁻²⁸ silver,^{29,30,31,32} and for dilute Au-Ag alloys³³ and the values obtained for E_f , E_m , etc., have been tabulated by Seeger and Schumacher.³⁴ The residual resistivity method, however, has some inherent disadvantages since it is extremely difficult to distinguish between the resistivity effects of point defects, impurity atoms, stacking faults, dislocations and grain boundaries within the specimen. For this reason a number of other

techniques have been devised for vacancy measurements in pure gold and silver. These include calorimetry,³⁵ mechanical properties³⁶⁻⁴⁴ thermoelectric effects,^{45,46,47} anelastic measurements,⁴⁸ dilatometry,^{49,50,51,26} and direct observation by transmission electron microscopy.^{52-60,17,18}

Although each method has its advantages and disadvantages, it was felt that the dilatometric method devised by Takamura,⁵⁰ coupled with concurrent transmission observations, best suited the objectives of the present study on the gold-silver system. In this investigation, single crystals of gold-silver alloys of various compositions were first grown and prepared as dilatometer specimens. The specimens were quenched from elevated temperatures near the melting point directly into ice brine and subsequently annealed in the dilatometer at room temperature. Similar dilatometer runs were performed for polycrystalline wire samples to note any grain boundary effect. The specimen size was also varied to note any possible size effect of the kind reported by Takamura^{50,18} and disputed by Jackson.^{18,61} Transmission microscopy was done on quenched alloy and pure metal foils in an effort to correlate the observed defect structure with the results obtained by dilatometry. A preliminary hardness study of quenched samples was also initiated.

The research described in this paper was part of a project at Ohio State University on interdiffusion in the gold-silver system. The

present results will be correlated later with transmission work on defect interaction in the diffusion zone and with diffusion couple data obtained by microprobe analysis.

EXPERIMENTAL PROCEDURE

Single crystals of pure gold and silver and Au-Ag alloys were grown from the melt by a modified Bridgeman technique. The crystal growing furnace is shown schematically in Figure 1 and represents a variation of the usual Bridgeman furnaces described by Lawson and others^{62, 63, 11} since the specimen crucible remains stationary rather than being pulled through the hot zone. The temperature gradient is instead produced by shunting the bottom Kanthal heating element and producing a vertical temperature gradient across the crucible by means of a timer and program unit. This stationary method provides the advantage of more uniform control and eliminates undesirable vibrations inherent in furnace pulley systems.

The control board for the furnace shown in Figure 2 consists of a Barber-Colman Model AE 2971 Program Unit, a Model 351 T Reference Voltage Source calibrated for 0-50 millivolts, a Model A 3139 Indicator Assembly with a null seeking zero galvanometer, and an Eagle Flexopulse repeat cycle timer. The program unit provides a dial for pre-setting a temperature at the start of the program. A motor driven potentiometer then changes the control set point (temperature) once the cooling cycle is begun. The Galvanometer in turn indicates the deviation between the set point voltage at the reference voltage source and the

actual voltage produced by the thermocouple at the base of the specimen crucible. The thermocouple in this case is a Thermo-Electric type K chromel-alumel one encased in ceramic with an outer sheath of Inconel. Each thermocouple was calibrated at the factory against a National Bureau of Standards reference source and deviations from the reference curve were certified at three points, 700°C, 900°C, and 1063°C.

The repeat cycle timer provides a continuous spectrum of slopes for cooling curves by continually interrupting the power to the Kanthal heating elements for preset intervals during the cooling cycle.

Both ends of the McDanel tube were sealed by water-cooled O-rings so that during the cooling cycle an oil diffusion pump in conjunction with a fore pump and liquid Nitrogen trap normally attained a vacuum of 5×10^{-5} mm Hg as indicated by a Philips type vacuum gauge.

One of the various types of crucibles used for growing dilatometer specimens is shown in Figure 3. The crucibles were machined from high purity CCV grade graphite which is a molded, fine grain graphite with a fine surface finish. The center split mold was bored with one mm or two mm diameter holes approximately 120 mm in depth and tapered at the bottom. The inside walls were carefully polished with 4/0 paper and cotton swabs to a smooth finish in order to prevent heterogeneous nucleation at surface irregularities. The entire crucible assembly rested on a chill rod of oxygen-free (OFHC) copper which provided directional cooling through the base of the graphite mold and insured that

Figure 1. Single Crystal Growing Furnace

Figure 2. Control Board and Wiring Diagram
for Crystal Furnace

Figure 3. Graphite Mold used to grow one mm
diameter single crystal dilatometer
specimens

nucleation would be initiated at the tip of the mold holes. Multiple mold holes were used in later runs and five crystals could be grown simultaneously. Further variations in mold core design produced three mm diameter crystals for diffusion couples and flat, rectangular (0.5 mm thick) specimens for hardness measurements.

The starting material for the single crystals was high purity (99.999%) gold and silver in both powder (-100 mesh) and wire (0.040 inch diameter) form. A typical analysis is shown in Table 1.

Table 1

Typical Analysis for Impurities in Gold and Silver

1. GOLD 99.999⁺%

Silver	less than 2PPM	(0.0002%)
Copper	" "	1PPM (0.0001%)
Iron	" "	1 PPM (0.0001%)
Magnesium	" "	1PPM (0.0001%)
Lead	" "	1PPM (0.0001%)
Silicon	" "	1PPM (0.0001%)

2. SILVER 99.999⁺%

Aluminum	1PPM	(0.0001%)
Copper	1PPM	(0.0001%)
Cadmium	1PPM	(0.0001%)
Lead	1PPM	(0.0001%)
Silicon	1PPM	(0.0001%)

Note: No other impurities were detected spectrographically.

Since the solubility of carbon in gold and silver is negligible,^{11, 64} and since all specimens were grown under vacuum, the single crystals in all probability maintained a purity close to that of the starting material. This was verified by wet chemical analysis of a 50 wt. % Au - 50 wt. % Ag crystal which showed a deviation of only 1/2% from starting composition, and by similar analysis along the length of Au-Ag alloy crystals by V. Ruth.¹¹ Laue X-ray patterns were also taken of the initial as-grown crystals to confirm the absence of polycrystalline grains. However, since any grain boundaries were clearly visible after etching, subsequent crystals were examined visually. The etching reagent found most suitable for silver and high silver alloys was a mixture of equal parts of hydrogen peroxide and ammonium hydroxide, while the pure gold specimens were given a light etch in aqua regia. The binary phase diagram for the system gold-silver is shown in Figure 4.

The as-grown single crystals were clamped in a felt-lined holder and both ends were carefully trimmed off with a jewelers saw. The ends of the crystals were then polished flat to a final length of 100 mm for the dilatometer specimens.

A number of two mm diameter crystals were also swaged down to one mm diameter wire and specimens of 100 mm length were cut and etched from this material.

The wire and crystal dilatometer specimens were heated to the desired quench temperature in the crystal furnace by means of graphite-

Figure 4. Equilibrium binary phase diagram
of the system gold-silver⁽⁶⁴⁾

tipped tongs which held the specimen suspended in an inert atmosphere of argon. Initially, dilatometer gold samples were heated in a commercial grade (99.995%) of argon gas which passed directly from the cylinder into the furnace. However, because of reports of the existence of water vapor in tanks of this grade, a much higher grade of Matheson ultra-high purity argon was substituted for subsequent runs. This gas was passed through purging bottles of magnesium perchlorate $\overline{\text{Mg}(\text{ClO}_4)_2}$, and anhydrous Drierite (CaSO_4) indicator before entering the furnace tube as an extra precautionary measure against water vapor. Each tank of ultra-high purity argon was analyzed at the plant and the bottle analysis for the first tank used is shown in Table 2.

Table 2

Analysis of Ultra Pure Argon, Ionization Grade (99.999% Min.)

Cylinder #48972

O_2	less than	5.0 PPM
N_2	" "	5.0 PPM
CH_4	" "	2.0 PPM
CO	" "	1.0 PPM
CO_2	" "	1.0 PPM
H_2	" "	1.0 PPM
H_2O	" "	1.5 PPM

To further minimize any possible effect of oxygen in the silver samples, the wire specimens were vacuum annealed at 550°C for one hour before they were used in the quench experiments.

After holding at the desired quench temperature the specimen was dropped vertically into a quench bath of iced brine at -11°C. A support of soft Pyrex glass wool at the bottom of the beaker prevented deformation of the soft crystals. The sample was then carried in the quench bath directly to the dilatometer apparatus which was located in a constant-temperature room across the hall. The quenched specimen was immersed into a bath of water kept in the room to bring the sample to room temperature. After about five to ten seconds, the specimen was gently blotted dry with lens tissue and carefully inserted into the Invar specimen block in the dilatometer as shown in Figure 5. An Invar plate was then fastened over the back of the specimen holder and a Lucite cover was placed over the entire dilatometer.

The length measurements were made visually through a transit telescope (Figure 6) which was focused on the scale reflected in the galvanometer mirror. As the excess vacancies diffused to sinks during the room temperature anneal, the specimen contracted and a set of springs followed this length contraction by pulling two small Invar blocks over a set of rollers. The galvanometer mirror rotated counter-clockwise, which in turn, reflected an upward motion on the vertical scale. This optical lever could detect length changes of 1×10^{-6} .

Figure 5. Cross-section of the dilatometer

Figure 6. Schematic view of the optical
dilatometer apparatus

A well-annealed specimen of the same composition was originally used to compensate for thermal expansion caused by room temperature fluctuations. However, it was extremely difficult to polish the ends of both the quenched and the annealed crystals to identical lengths because of their extremely high ductility. Therefore, the annealed reference specimen was removed and, instead, a two foot thick foam insulation was placed over the Lucite for further temperature control. This worked quite well and the dilatometer temperature fluctuations rarely exceeded $\pm 0.1^{\circ}\text{C}$ and generally remained within $\pm 0.05^{\circ}\text{C}$ for the first few hundred minutes of the run when most of the vacancy annealing occurred.

The initial calibration runs with the dilatometer produced some anomalous observations including an apparent steady and persistent specimen expansion.

As a test, a two mm diameter rod of steel was substituted for the quenched crystals in the dilatometer. The length of the steel specimen responded as expected to fluctuations in room temperature, thereby indicating that the dilatometer itself was functioning satisfactorily. The ambiguous results were apparently caused by deformation of the ductile crystals from an excessive spring load. This was remedied by replacing the steel springs with much softer phosphor-bronze ones, placing a quartz tube sheath in the Invar specimen holder, and inserting a nylon tip on the end of the small roller bars. These modifications succeeded

in eliminating the spurious expansion effects. This was confirmed by observing a quenched gold wire for a period of more than 50,000 minutes (approximately 35 days); during the entire run there was no evidence of specimen deformation.

The reproducibility of the dilatometer data was also checked by making three identical quenches with gold wires from 900°C. The same initial rapid contraction rate and final total length contraction were observed in each instance.

Although a total of approximately 110 dilatometer specimens were quenched, a number of these were used for calibration tests, while other results were rejected because of accidental deformation during handling or because of room temperature fluctuations due to faulty air-conditioning control.

The thin films for the transmission studies were prepared from 0.07 mm thick foils rolled from the one mm diameter wires. The foils were quenched in the same manner as the dilatometer specimens into a brine bath at -10°C and either annealed at room temperature or transferred immediately to a beaker of boiling water and aged at 100°C for 30 - 60 minutes.

After a minimum of 24 hours at room temperature, the foils were electrolytically thinned in a bath of 34 grams potassium cyanide, 7.5 grams potassium ferrocyanide, 7.5 grams potassium sodium tartrate, two cm³ phosphoric acid, two cm³ ammonia and 500 cm³

water.⁵² The thinning unit used was devised by Glenn at the Bain Research Laboratories and is shown in Figure 7. The "window" technique^{17, 65} of thinning was employed with a coating of Microstop lacquer around the specimen edges to prevent edge attack. The foil was placed between the hollow cathodes and an impeller was turned on to provide a stream of electrolyte impinging on the immersed specimen from both sides. The current utilized during polishing was 3000 MA at 20 volts.

After thinning, the specimen was rinsed in distilled water and clean methyl alcohol. The thin sections were cut out with a sharp scalpel on a plastic block immersed in methyl alcohol. The thin areas were then mounted on 75-mesh copper grids for support, placed in the specimen holders and examined at 100 kv in the Philips 100 EM electron microscope. The photographic film used was 35 mm Kodak fine grain Positive and approximately 20 - 30 pictures were taken of varied areas in each specimen. A total of about 500 negatives were produced and examined after printing.

Figure 7. Two views of Glenn Electropolishing Unit. Specimen is shown in lower view at (S) held between two hollow cathodes (C). Water (W) was used as coolant for electrolytic bath.

RESULTS AND DISCUSSION

Pure Gold

A vacancy is formed by removing an atom from the interior of a crystal and bringing it to the surface, thereby increasing the volume of the crystal and correspondingly decreasing its density. Similarly, a crystal which has retained a supersaturation of vacancies within its lattice by a rapid quench from elevated temperatures will undergo a contraction in length as these vacancies are annihilated at sinks during annealing. The relation between this length contraction and the equilibrium concentration of vacancies can be derived in the following manner:

The Gibbs free energy, F_v , of a crystal containing n vacancies is given by:

$$F_v = nE_f + pv - TS_v$$

where E_f is the energy of formation of a single vacancy

S_v is the entropy due to vacancies.

The pressure-volume term changes negligibly with vacancy concentration and this can be neglected in a variational problem. The entropy, S_v , is actually composed of two terms, a vibrational entropy and an entropy of mixing, but the vibrational contribution to the entropy increase is of

secondary importance. The configurational entropy of mixing is given by

$$S = k \ln W = k \ln \frac{N!}{(N-n)!n!}$$

where N is the total available lattice sites

So that the free energy becomes:

$$F = nE_F - kT \ln \frac{N!}{(N-n)!n!}$$

applying Stirling's formula for the logarithm of the factorial of a large number:

$$\ln x! \approx x \ln x - x$$

$$F = nE_F - kT [N \ln N - (N-n) \ln (N-n) - n \ln n]$$

The condition of thermodynamic equilibrium within the lattice is given by minimizing the free energy with respect to the number of vacancies.

Then,

$$\frac{\partial F}{\partial n} = 0 = E_F - kT \left(\ln \frac{N-n}{n} \right)$$

$$\frac{n}{(N-n)} = \exp^{-E_F/kT}$$

if $n \ll N$

$$\frac{n}{N} = \exp^{-E_F/kT}$$

and if we include the vibrational entropy in a pre-exponential term A we have:

$$\frac{n}{N} = A \exp^{-E_F/kT}$$

Finally, assuming that a quenched metal contracts isotropically by the annihilation of excess vacancies, then the concentration of vacancies at the quench temperature is related by the following equation:

$$\alpha \frac{n}{N} = \alpha C_D = \frac{\Delta V_T}{V} = 3 \frac{\Delta L}{L} = A \exp^{-E_F/kT_q}$$

where: C_D = vacancy concentration at the elevated temperature from which the quench was made

α = fractional volume of a single vacancy

$\frac{\Delta V_T}{V}$ = total volume change exhibited by the specimen

$\frac{\Delta L}{L}$ = fractional length change measured by dilatometer

E_F = formation energy of a vacancy

k = Boltzmann constant

T_q = temperature from which the quench was made

A = pre-exponential entropy factor.

From this equation both the energy required to form a vacancy within a crystal lattice and the number of vacancies in equilibrium at the quench temperature can be deduced from length measurements of the specimen contraction during annealing. The validity of the experimental results of course is dependent on a number of factors including the assumption that all of the excess vacancies migrate to types of sinks such as the surface, grain boundaries, or vacancy precipitates which

totally annihilate the vacancy, thereby producing a length contraction. If, however, some of the quenched-in vacancies remain bound to impurity atoms or coalesce into clusters with little or no lattice relaxation, then the length measurements will result in vacancy concentrations which are lower than the actual equilibrium values. For this reason the dilatometer measurements were coupled with transmission electron microscopy to directly observe, if possible, the predominant type of vacancy sink in pure Au (99.999%), pure Ag (99.999+%), and Au-Ag alloys of various compositions.

The results of the dilatometer measurements in pure gold are compiled in figures 8 to 10 as a plot of the observed fractional change in specimen length ($\Delta L/L$) versus the annealing time at room temperature. The deduced volume change ($\Delta V/V$) is also represented on the ordinate axis. Although Lazerev⁵¹ criticized the simple volume to length relationship ($\Delta V/V = 3(\Delta L/L)$), mainly on the failure of his tubular dilatometer specimens, Gertsriken⁶⁶ has upheld its validity with his own measurements and those of Baurle and Koehler.⁶⁷

The first result to be noted from the current dilatometer observations is that the total amount of contraction increased with increasing quench temperature for the specimens quenched from temperatures above about 900°C. This, of course, is the result expected if the observed contraction in specimen length is due to the annihilation of quenched-in vacancies since the equilibrium vacancy concentration

Figures 8, 9, 10. Dilatometer annealing curves for pure
gold specimens

T_q = quench temperature

T_A = annealing temperature
(20°C for all dilatometer
specimens)

L = original length of dilatometer
specimens (100 mm)

Figure 11. Total observed volume change of
dilatometer gold specimens versus
reciprocal of quench temperature

increases with increasing temperature, as shown previously by the exponential equation. This is also shown in the compilation of vacancy concentration in Table III.

The values of C_D , the vacancy concentration computed from length contraction, are dependent on the choice of α , the volume of a single vacancy. Although some early investigators⁶⁶ utilized a value of unity for vacancy volume, there is some relaxation of atoms about a vacant site in an atomic lattice so that theoretical values of α in the fcc metals range from 0.4 to 0.98.^{50, 16, 18} The value of $\alpha = 0.43$ for gold was obtained by Takamura⁵⁰ and vacancy concentrations using this value are shown in Table III for all of the dilatometer runs. However, Takamura's value was obtained by combining resistivity values with dilatometer contraction results. The present dilatometer experiments for pure gold wires show a greater total contraction indicating that Takamura's specimens suffered somewhat greater vacancy loss during quenching than the current results.

A much better technique to directly determine the activation volume of formation is to measure the quenched-in electrical resistance as a function of gas pressure on a metal. The Gibbs free energy due to

TABLE 3

Vacancy Concentration Deduced from Dilatometer Measurements

Composition	T_q (°C)	$\Delta V/V$ ($\times 10^{-5}$)	C_D ($\alpha = .43$) ($\times 10^{-4}$)	C_D ($\alpha = .525$) ($\times 10^{-4}$)	C (Simmons & Balluffi) ($\times 10^{-4}$)	E_F (ev)	E_F (Simmons & Balluffi) (ev)
Pure Au	1025	27.0	6.3	5.15	6.0		
Wires	1000	20.58	4.8	3.9	4.8		
(Dry Argon	950	18.39	4.3	3.5	3.3	0.71	.94
Atmosphere)	925	14.1	3.3	2.5	2.6		
	875	11.25	2.6	2.1	-		
	600	0.75	0.018	0.014	-		
Pure Au	1050	24.6	5.7	4.7	6.8		
Wires	1000	17.58	4.1	3.4	4.8		
(Commercial	950	9.9	2.3	1.89	3.3	1.42	
Argon)	925	7.5	1.75	1.46	2.6		
	900	5.40	1.25	1.03	2.3		
	900	5.25	1.22	1.00	2.3		
	900	5.25	1.22	1.00	2.3		
Pure Au	1050	13.5	3.3	2.57	6.8		
Single	1000	11.25	2.6	2.14	4.8	0.85	
Crystals	975	7.25	1.7	1.38	4.0		
	900	5.4	1.25	1.03	2.3		
80%Au	1025	12.8	3.0	2.44			
Wires	1000	9.3	2.15	1.77			
	950	4.23	0.99	0.81			
	900	2.61	0.61	0.50		1.68	

Table 3 (contd.)

Composition	T_q (°C)	$\Delta V/V$ ($\times 10^{-5}$)	C_D ($\alpha = .43$) ($\times 10^{-4}$)	C_D ($\alpha = .525$) ($\times 10^{-4}$)	C (Simmons & Balluffi) ($\times 10^{-4}$)	E_F (ev)	E_F (Simmons & Balluffi) (ev)
	850	6.72	1.56	1.28			
	700	7.5	1.74	1.49			
	600	10.45	2.44	2.60			
	400	3.78	0.88	0.72			
80%Au	1025	12.0	2.9	2.28			
Crystals	975	7.8	1.8	1.5			
	950	2.4	0.56	0.46		2.69	
	800	5.58	1.3	1.06			
	600	7.5	1.75	1.43			
60%Au	1000	8.64	2.0	1.65			
Wires	900	6.75	1.57	1.30			
	700	1.87	0.43	0.35			
	600	4.2	0.98	0.80			
60%Au	1010	6.0	1.4	1.14			
Crystals	1000	4.8	1.1	0.91		3.39	
	950	1.32	0.31	0.25			
	600	7.35	1.7	1.4			
20%Au	950	1.05	0.24	0.20			
Wire							
Pure Ag	950	no contraction observed			1.7		1.09
	to				(at melting		
	600				point 960°C)		

formation of n lattice vacancies in a perfect crystal containing N similar atoms at constant pressure p and constant temperature T is given by:

$$\Delta G_{f(n, p, t)} = n \Delta E_f + np \Delta V_f - nT \Delta S_f^{\text{vib}} - kT \ln \frac{N!}{(N-n)! n!}$$

where E_f = internal energy change for vacancy formation

V_f = volume change

S_f = vibrational entropy change

k = Boltzmann constant

The equilibrium condition is:

$$\left(\frac{\partial \Delta G_f}{\partial n} \right)_{p, T} = 0$$

which in conjunction with Stirling's formula yields:

$$C_{(p, T)} = \exp \frac{[\Delta S_f^{\text{vib}}/k]}{\exp \frac{[\Delta E_f + P \Delta V_f]}{kT}}$$

The activation volume of formation ΔV_f can then be directly obtained by measuring some experimental parameter, such as electrical resistance, which is directly proportional to C , the vacancy concentration, as a function of hydrostatic pressure within a high pressure gas cell. A recent experiment of this type on gold by R. P. Huebener^{68,69} has produced a value of 0.53 ± 0.04 for ΔV_f and 0.15 ± 0.014 for ΔV_m , the migration activation volume. Since the total activation volume of self-diffusion is the sum of the formation volume and the migration volume, his experimental values yield an activation volume for self-diffusion in gold of:

$$(\Delta V_f + \Delta V_m) = (.53 + .15) = .68 \pm .05$$

Figure 12 (top). Vacancy concentration versus reciprocal of quench temperature. The dotted line represents the equilibrium values obtained by Simmons and Balluffi (Reference 15)

Figure 13 (bottom). Volume change versus dilatometer specimen diameter. (Reproduced from Reference 18, p. 547, Figure 15)

Relation between the specimen size and the concentrations of the total vacancies and of thermal vacancies, for gold brine-quenched from 850°C . The concentrations were deduced from the length contraction measurements, assuming the fractional volume of a vacancy to be 0.43, (Takamura)

which is in excellent agreement with the self-diffusion data of Tomizuka, et al.⁷⁰ A similar formation volume of 0.52 ± 0.07 has also recently been reported by Grimes.⁷¹

The concentration of vacancies as measured by the current dilatometer experiments were calculated using both Huebener's and Takamura's values for vacancy volume and the results for pure gold wires heated in dry argon are shown in Figure 12 for comparison. The dotted line represents the equilibrium vacancy concentration for pure gold as measured by Simmons and Balluffi.¹⁵ Their method of vacancy concentration measurement was by simultaneously measuring the temperature dependence of the length change and the lattice constant while at elevated temperatures.

From the relationship

$$\left(\frac{\Delta N}{N} \right)_T = 3 \left(\frac{\Delta L}{L} - \frac{\Delta a}{a} \right)$$

where $\Delta N/N$ is the defect population at temperature T

$\Delta L/L$ is the length change

$\Delta a/a$ is the lattice parameter change.

Simmons and Balluffi found that $\Delta N/N$ was always positive, indicating that the point defects were vacant lattice sites rather than interstitials. Since this method requires exacting measurements of the length and lattice parameters while actually at the elevated temperatures, their data is generally regarded as more reliable than concentrations measured by quenching techniques where there is a chance of some

vacancy loss. If this is the case, then the present results for gold vacancy concentration are seen in Figure 12 to be in very good agreement with the data of Simmons and Balluffi, especially for values calculated with the new Huebener value of $\alpha = 0.53$. (Simmons and Balluffi themselves report possible experimental errors in their curve of about 8% at the highest temperature and 25% at the lowest temperature.) In the same paper, they also computed $\alpha = 0.45$ but this was based on the length measurements of Takamura and, as mentioned before, his values are slightly lower than the present results, hence, their value of 0.45 is lower than Huebener's. At any rate, if the Simmons and Balluffi curve for gold is very close to the actual equilibrium concentrations at these temperatures, then the current dilatometer measurements suggest that 0.53 is the better value for the fractional volume of a vacancy. This also strongly indicates that Seeger's, et al.⁷² activation volume of 0.98 for gold is too high.

The dilatometer annealing curves also display rapid initial specimen contraction in the first few hundred minutes of anneal time with little subsequent change. This rapid steady decay differs from the usual "S"-shaped resistivity annealing curves which exhibit slow then rapid decay rates.²⁰ While Takamura⁵⁰ attributed this difference to the lattice relaxation caused by the formation of some types of clusters which are not detected by resistivity, it is more likely that the consistent

contraction is produced by the continual disappearance of quenched-in vacancies at sinks. This large amount of steady specimen contraction also rules out the possibility that the excess vacancies are aggregating to voids during the annealing process at room temperature.

The predominant sink in pure gold quenched from 1000°C and annealed at 20°C turns out to be the famous "black spot" defect as revealed in the transmission photomicrograph of Figure 14. This type of vacancy precipitate was first noted by Cotterill^{73,27} and there has been such a considerable amount of subsequent conjecture as to its exact nature and role in quenched metals that it has been labeled the "black death" by J. S. Koehler.⁷⁴

The spot defects in Figure 14 are generally less than $75\text{\AA}$ in diameter and unresolvable, although a few larger precipitates appear to have a triangular shape as shown in region (A). The specimen shown in this photomicrograph was aged at room temperature for one week after quenching so that the defect structure shown would correspond to a point on the dilatometer curves for pure gold where contraction has ceased. The density of spots is approximately $1 \times 10^{15} \text{ cm}^{-3}$. This can be compared with a density of $5 \times 10^{14} \text{ cm}^{-3}$ of $25\text{\AA}$ diameter spots reported by Cotterill⁷³ for a gold specimen quenched from 930°C into ice water at 0°C and annealed for only 60 seconds at room temperature. The fact that Cotterill noted a lower density of smaller black spots within the first minute after quench implies that the defects grew by the

Figure 14. "Black Spot" vacancy precipitates
in pure (99.999%) gold foil quenched
from a dry argon furnace atmosphere
at 1000°C into brine at -11°C and
annealed at 20°C for one week
magnification (58,000X)

subsequent absorption of excess vacancies as annealing progressed to the final stage represented in Figure 14. This assumption is consistent with the steady and rapid decay of the dilatometer curves for the gold specimen. Since the first minute of anneal time was missed during the insertion of each dilatometer specimen there were no measurements of contraction prior to black spot formation such as those noted by Takamura and Greenfield.⁷⁵ These authors observed a period of accelerated specimen contraction associated with the appearance of black spots after 200 minutes of anneal time in a 0.5 at. % Mg-Al alloy quenched from 600°C.

In an effort to unravel the identity of these black spots, a gold specimen was quenched from 1000°C into brine at -10°C and annealed for 12 hours to allow the formation of black spot defects. The growth of these precipitates was then accelerated by immersing the foil in boiling water for two hours. The resulting defect structure is shown in Figure 15. Some of the unresolvable spot defects have grown into large and distinct stacking-fault tetrahedra up to 500⁰Å in size as shown in regions (A), (B) and (C). Intermediate sizes of tetrahedra are also clearly evident as at (D) and (E) while black spots down to 50⁰Å are visible throughout the background. The density of spots remains approximately the same as the fully aged room temperature condition in Figure 14.

Figure 15. Pure gold quenched from 1000°C , aged at 20°C for 12 hours and re-annealed at 100°C for two hours. Note the distinct tetrahedra at regions marked (A), (B), (C). Smaller triangular shaped precipitates appear at (D) and (E) while background shows still smaller spot defects.

(52,000X)

These stacking-fault tetrahedra were first discovered by Silcox and Hirsch in 1958 and analyzed as consisting of four triangular intrinsic stacking-faults on four non-parallel (111) planes arranged in tetrahedral shape. The edges of the tetrahedra are parallel to the six $\langle 110 \rangle$ directions and are formed by stair-rod dislocations with Burgers vectors $1/6 \langle 110 \rangle$. The authors pointed out that the photographic contrast of the tetrahedra is always dark relative to the background rather than the opposite effect which would be expected if the triangular defects were in reality merely crystallographic etching effects.

An even better examination of these stacking-fault tetrahedra can be made if the gold ribbon is immediately transferred to boiling water after quenching into brine. Figure 16 shows stacking-fault tetrahedra about $300\text{\AA}$ in average size in pure gold quenched from 1025°C and annealed at 100°C for one hour. This photo is a particularly good example of the precipitate denuded zone along the intersection of three grain boundaries. The grain boundaries act as very efficient annihilation sinks for migrating vacancies and hence sweep the surrounding area of excess vacancies during the quench. Hence no supersaturation of vacancies exists along the grain boundaries during the anneal and vacancy precipitation cannot occur in this zone. The denuded zone is also shown in Figure 17 at higher magnification. The straight lines on

Figure 16. Gold quenched from 1025°C and aged directly at 100°C for one hour. Note that the area around the intersecting grain boundaries is free of tetrahedra precipitates.

(43,000X)

Figure 17. Another view of a denuded zone
along grain boundary in quenched
gold. This foil was obtained from
the same quenched ribbon shown in
Figure 16. The straight lines in
the right portion of the photo are
microcracks

(120,000X)

the other side of the grain are microcracks emanating from the edge of the foil a short distance to the right of the photo. Note that these advancing microcracks are effectively blocked by the grain boundary.

The width of this denuded zone was measured to be about $0.4 - 0.5 \mu$, and since the zone width is dependent upon the quenching rate, this is comparable to the 0.4μ width reported by Meshii for a gold specimen quenched at $80,000^\circ\text{C}/\text{sec}$.⁷⁵

A similar precipitate-free zone is found immediately beneath the surface since the surface is also a vacancy sink during quenching. This surface loss prior to annealing may have been the cause of the lack of specimen contraction with the hollow, tubular dilatometer specimens utilized by Lazerev. R. L. Segall has also shown evidence in pure gold that coherent annealing twin boundaries act as very effective vacancy sinks and produce a denuded region about $5000\text{\AA}$ wide.⁷⁶ Dislocations which are present prior to the condition of vacancy supersaturation may also attract vacancies,⁵⁵ although precipitate-free zones about dislocations were not seen in any of the foils examined in the current work.

The foils were quenched from elevated temperatures well above the recrystallization temperature of 200°C for gold and silver⁷⁷ and the few regions of dislocations that were observed appeared to have been introduced during the scapel cutting or handling of the foil. The interaction between these dislocations and the vacancy precipitates will be discussed later.

The fact that the majority of vacancies in equilibrium at these elevated temperatures did not disappear to grain boundary sinks, etc., during quenching, but rather were retained in the metal lattice is evident from the extraordinary density of tetrahedra seen in Figure 18. The density of defect tetrahedra in this low magnification photo is about $3 \times 10^{15}/\text{cm}^3$ and is visual proof of the important role of vacancies in quenched face-centered cubic metals on metal properties.

If, however, the gold specimen is quenched from 600°C instead of 1000°C and then annealed at 100°C , a striking decrease in the size and density of vacancy precipitate occurs. The low density ($0.37 \times 10^{15}/\text{cm}^3$) of small black spots ($\sim 50\text{\AA} - 75\text{\AA}$ in size) in Figure 19 is in stark contrast to Figure 18 at much lower magnification. The black spots resulting from the 600°C quench are not distinguishable as tetrahedra even at a magnification of 127,000X (Figure 20). Note that the very low defect concentration evident from these photos corresponds to the small dilatometer length contraction shown in Figure 8 for the pure gold wire quenched from 600°C . The present transmission results with 100°C anneals correlate with the data of Cotterill who noted tetrahedra for specimens quenched from 1000°C , only black spot defects for 750°C quenches, and a mixture of black spots and tetrahedra for gold quenched from 800°C .⁷³ The black spots noted in the room temperature anneal for gold quenched from 1000°C is also consistent with the spot defects and very small tetrahedra observed by Clarebrough,

Figure 18. Density of stacking-fault tetrahedra in gold.

$T_q = 1025^{\circ}\text{C}$. $T_A = 100^{\circ}\text{C}$. The shapes of the precipitates cannot be resolved at this low magnification, but this foil region is close to that shown in Figure 16

(32,000X)

Figure 19. Pure gold quenched from 600°C and annealed at 100°C. Note the very low density of small precipitates as compared with high temperature quenches in previous figures. The broad parallel lines are stacking-fault fringes of extended dislocations.

(86, 500X)

Figure 20. Same gold foil as in Figure 19 only at
higher magnification. Precipitates still
cannot be resolved.

(127,000X)

et al. for rapid quenches from 1030°C.³² Although Clarebrough³² and Cotterill⁷³ suggested that the spot defects were perhaps small, spherically symmetric aggregates of vacancies, the present dilatometer measurements contradict this. The large amount of contraction and the deduced vacancy concentration in agreement with the Simmons and Balluffi data, instead point to a vacancy precipitate which totally annihilates the excess vacancies. The growth of distinct stacking-fault tetrahedra from the spot defects in Figure 15 also strongly implies that the black spots are in reality very small tetrahedra.

At this point it may be pertinent to review the two current mechanisms proposed for the nucleation and growth of stacking-fault tetrahedra in gold. The original mechanism proposed by Silcox and Hirsch is shown in the sketch in Figure 21. In this theory, the excess vacancies retained by quenching (Figure 21 (a)), coalesce to homogeneously nucleate a disk on a lattice plane (b). The disk of vacancies then collapses to form a prismatic dislocation loop if the energy of dislocation loop is less than that of the disk (c). Every segment of this dislocation loop is a pure edge dislocation with a Burgers vector of $1/3 a \langle 111 \rangle$ containing an intrinsic stacking-fault. The faulted loop is sessile and can only climb. If the vacancies condensed on a (111) plane in the form of an equilateral triangle with edges parallel

Figure 21. Silcox-Hirsch mechanism of
stacking-fault tetrahedra formation

to the $\langle 110 \rangle$ directions, the dislocation loop follows these edges and the resulting Burgers vector is αA in the notation of Thompson.^{78,79}

The triangular loop then dissociates into a stair rod and partial dislocation according to the reactions:

These are reactions of the type:

Frank sessile stair rod Shockley partial

and hence are energetically favorable. Figure 21 (d) shows the partials

βA , γA , δA bowing out on their (111) glide planes. Silcox and

Hirsch pointed out that the partials attract each other in pairs to form

stair-rod dislocations along DA, BA and CA according to the reactions:

which are also energetically favorable. This reaction is of the type

The result in Figure 21 (f) is a tetrahedron of stacking-faults on (111)

planes with an energy proportional to $6 \times 1/18 = 1/3$ as compared with

$3 \times 1/3 = 1$ for the original Frank prismatic triangle.

M. de Jong and J. S. Koehler²³, however, criticized this model on the grounds that the disks and loops expected prior to tetrahedra growth were not observed by electron microscopy in quenched and annealed gold. Instead, these authors proposed that the vacancies aggregate to a small nucleus which has a tetrahedral shape directly in the beginning of the process. The tetrahedron then grows by the absorption of vacancies at the stair-rod dislocation edges or corners which displaces a row of atoms over $a/6 \langle 112 \rangle$, thus creating a ledge in the face of the tetrahedron. Absorption of another vacancy at the favorable site created by the ledge will continue to increase the size of tetrahedra. This mechanism thus eliminates the intermediate step of prismatic loops. The mechanism has been further refined by D. Kuhlmann-Wilsdorf⁸⁰, who pointed out that the type of ledge (two are possible) formed is important.

The present transmission observations on quenched gold, along with that of Cotterill, Meshii, Maddin, Silcox and Hirsch, etc. (which are summarized in Reference 18), failed to reveal any type of vacancy precipitate other than stacking-fault tetrahedra and black spot defects for 100°C anneal temperatures. This would tend to support de Jong's mechanism of tetrahedra formation.

Still further evidence can be found in the vacancy concentrations deduced from the density of precipitates observed in the electron transmission photomicrographs. These are tabulated in Table 4. The

TABLE 4

Vacancy Concentration Deduced from Precipitate Density

(wt. %Au)	T _q (°C)	T _A (°C)	C _T (x10 ¹⁵ /cm ³)	$\bar{L}$ ₀ (Å)	C _v ^(a) (x10 ⁻⁴)	C _D ^(b) (x10 ⁻⁴)
100	1025	100	2.5	250	1.6	5.15
100(c)	1000	100	1.8	275	1.2	4
100(d)	1000	100	1.49	270	1.10	-
100	1000	20	1.5	>100	0.3	3.9
100	600	100	0.4	~50	0.01	0.075
80	1000	100	5.6	150	1.3	1.8
80	1000	20	4.0	<100	0.4	1.8
80	600	100	1.4	~200	0.6	2.6
60	1000	100	3.0	<150	0.7	1.65
100	1000	20	1.0	100	0.9	3.9
		then 100		to 500		

$$(a) C_v = \frac{\bar{L}^2 C_T}{4}$$

(b) All C_D values calculated using $\alpha = 0.53$ (Table 3) for wire specimens aged at 20°C.

(c) Furnace atmosphere of commercial argon.

(d) Furnace atmosphere of air (Cotterill).⁷³

Note: All other specimens heated in dry argon.

foils were assumed to be $1000\text{\AA}$ thick, similar to those measured by Silcox and Hirsch. It must be pointed out that caution should be exercised whenever vacancy concentrations are based on vacancy defect density since there are deviations in size and density of tetrahedra within any single specimen foil.⁸¹ The counts were made on pictures which possessed the greatest amount of clarity and resolution and these may not have been truly representative of the entire foil or the larger dilatometer specimens. Furthermore, spots much smaller than about $50\text{\AA}$ could often not be detected with the Phillips microscope. Nonetheless, the table does give an indication of the vacancy concentration variations with quench and annealing temperatures.

Furthermore, the data can be compared with that of Cotterill⁷³ who presumed that the mechanism of tetrahedra formation was that of vacancy disk collapse-prismatic loop-tetrahedra.

In his paper the vacancy concentration from defect density is equal to

$$C_v = L^2 C_T a/4$$

where L = length of the tetrahedra sides

C_T = density of tetrahedra

a = lattice parameter.

For a quench from 1000°C and an anneal at 100°C , he calculated from density measurements a vacancy concentration of 1.1×10^{-4} . The present data shown in Table 4 for pure gold quenched from 1000°C and

annealed at 100°C is in very good agreement with Cotterill's calculations. Note that the low concentration of black spots for the 600°C quenched foil is in agreement with the small amount of contraction produced by gold dilatometer specimens quenched from the same temperature. The observation of vacancy precipitates at this low quench temperature confirms the predictions of Kauffman and Meshii that stable clusters should be formed for quenches as low as 600°C and down to 500°C where the majority of vacancies migrate to fixed sinks instead of clusters.⁸²

Both the dilatometer annealing curves and the typical S-shaped resistivity curve can be qualitatively explained if the tetrahedra grow by the successive absorption of vacancies. Maddin et al.⁵⁶ have explained the resistivity curve on the basis of a constant density of tetrahedra observed during the progress of annealing. According to these authors, at the beginning of annealing, there is a maximum number of available vacancies but a minimum number of sinks since the tetrahedra are still small. Therefore, the rate of growth and its effect on resistivity will be small. As the tetrahedra grow in size the amount of ledge sinks increase and the growth rate also increases. In the latter stages of aging, the number of sinks is large but few excess vacancies are left so that the growth rate is again slow.

Both Clarebrough and Cotterill observed that the nucleation of small tetrahedra is a very rapid process and is completed in the very early stages (less than one minute) of annealing even at temperature

below 100°C. The time required to insert a specimen into the dilatometer and begin the first length measurement was on the average of two to four minutes so that only the growth stages of annealing were detected by this method. The observed dilatometer curves were extrapolated to one minute of anneal time on a semi-logarithm plot of time versus contraction and the missed contraction was added to the total. However, this missed contraction was very small and generally less than five percent of the total.

Although the majority of evidence thus far in quenched gold points to the de Jong mechanism of formation, a recent study by Clarebrough and Segall³² has added some perplexity to the problem. Pure gold specimens were quenched from 1030°C into ice water at 0°C and transferred to liquid nitrogen and then up-quenched to 100°C. The resulting defects included both tetrahedra and 3, 4, 5, and 6 sided prismatic dislocation loops. The existence of these loops in conjunction with stacking-fault tetrahedra has been suggested by Kuhlmann-Wilsdorf⁸³ as evidence that the tetrahedra can form fully grown by the Silcox-Hirsch mechanism in addition to their gradual growth from small vacancy clusters. Exactly why the observations of Clarebrough deviate from those of Silcox and Hirsch, Cotterill, etc., and the present study is not clear. Although variations in pre-aging time between the quench bath and the aging bath have been previously known to alter the size and density of tetrahedra,⁵⁷ this type of experimental difference has not

produced loops. Perhaps undetected impurities in the gold may also have contributed to this deviation.

It should be reiterated that there are two distinct processes involved: nucleation and growth. A number of authors¹⁸ have presented energy calculations based on homogeneous nucleation to predict the type of vacancy aggregate which should be present at a given supersaturation of vacancies. Cotterill²⁷ has also suggested that homogeneous nucleation is predominant above a critical temperature, T_{crit} , which is about 825°C for 99.999% gold and which is decreased with a decrease in impurity concentration. The large tetrahedra would then be the result of homogeneous nucleation while the spot defects were formed by heterogeneous nucleation.⁸⁴

Cotterill's proposal is a moot one for recent work by Davis and Hirth⁸⁵ shows a large discrepancy between the calculated homogeneous nucleation rates of dislocation loops and those observed experimentally. This implies that all observed vacancy clusters are nucleated heterogeneously on impurities. Homogeneous nucleation of vacancy precipitates is ruled out as are the predictions and calculations based on homogeneous nucleation models. The authors go on to point out that if nucleation occurs at impurities, the impurities can be decisive in determining the expected cluster type. This prediction is borne out by Ytterhus and Balluffi who observed that essentially all of the excess vacancies were annihilated at heterogeneously nucleated sinks after quenching gold from 700°C.²⁵

Impurities apparently affected the results of even the 99.999% purity gold when the dilatometer specimens were heated in a furnace atmosphere of a commercial grade of argon rather than the dried, ultra-pure type normally utilized in the quenching apparatus. Figure 9 shows that the gold wires consistently produced less total contraction when quenched from the impure argon. The transmission photos in Figures 22 and 23 similarly reveal a decrease in the density of stacking-fault tetrahedra (Table 4). This reduction in defect density is in agreement with the marked reduction in tetrahedra density and much larger tetrahedra size observed by Clarebrough²⁸ for gold specimens pre-treated in pure oxygen as compared with those pre-treated in carbon monoxide prior to quenching.

Jeannotte and Machlin had originally studied the influence of pre-treating gold in helium and helium-oxygen mixtures on the resistivity curves during annealing.²⁴ They attributed the differences in resistivity behavior after quenching from the two types of atmospheres to an interaction between vacancies and oxygen atoms in solution and suggested that the solubility of oxygen in gold is appreciable. This suggestion is not in agreement with the low solubility measured by others.^{86, 87, 88} It is more likely that the increased density of vacancy precipitates for the dry argon or carbon monoxide atmosphere reflects a higher nucleation rate of vacancies on impurities which are present even in 99.999% gold. The high nucleation rate due to available impurity

Figure 22. Stacking-fault tetrahedra in pure gold quenched from a furnace atmosphere of commercial argon at 1000°C into brine at -6°C and annealed at 100°C for 45 minutes. The triangular shapes of the tetrahedra along the $\langle 110 \rangle$ directions are very clear in this photo. Note the arrangement of some tetrahedra in pairs at regions marked (A).

(83,000X)

Figure 23. Same foil as in Figure 22. A denuded zone is shown at the intersection of three grain boundaries. The grain in the lower left has scattered the incident microscope electron beam out of the aperture and consequently appears dark.

(63,000X)

sites in conjunction with a limited amount of quenched-in vacancies, would produce smaller tetrahedra with a high density. On the other hand, heating the gold specimen in air, impure argon, etc., could remove the impurity atoms by oxidation. This would decrease the amount of heterogeneous nucleation sites and thereby produce fewer tetrahedra of larger size. The gas impurity in the case of the commercial argon was probably water vapor since the gas content is known to vary from one individual tank to another. Clarebrough also studied the effect on resistivity of quenching from argon which had been bubbled through water in a wash bottle and found the annealing behavior of silver was similar to that of air heating but markedly different from carbon monoxide atmospheres.²⁸

Ytterhus and Balluffi have suggested four possibilities for the removal of impurities in gold when heated in the presence of oxygen atoms: (1) evaporation loss at the surface; (2) formation of impurity oxides at the surface; (3) internal oxidation; (4) impurity clustering at grain boundaries. On the basis of their resistivity annealing curves²⁵ they felt internal oxidation or impurity clustering were the logical choice. However, Gegel observed no internal oxidation in gold doped with indium when heated in air at 850° - 950°C for 25 hours.⁴⁷ He did note a surface discoloration on a 99.995% gold sample after annealing, indicating that oxidation occurred only at the surface. Further work is required in this area.

The exact manner in which the impurity atoms promote tetrahedra nucleation is not known. Even the identity of the impurities which are responsible is masked. Silver is the chief impurity in the 99.999% gold utilized in the current investigations (Table 1), but Meshii found that the density of stacking-fault tetrahedra is the same for pure (99.999%) gold as for gold doped with additions of 0.5 at. % and 0.1 at. % silver.⁸⁹ Furthermore, neither copper nor iron were found to enhance or suppress the nucleation of tetrahedral stacking-faults in gold.

Although it is expected that impurities with large binding energies between the atom and vacancies will provide the largest effect on vacancy precipitation, very few measurements have been made of vacancy-impurity binding energies.

The amount of energy, E_F^i , required to remove an atom which is a nearest neighbor to an impurity and place it on the surface is the difference between the energy of formation of vacancy, E_F^v , and the binding energy, B_{i-v} , of a vacancy to an impurity atom.

$$E_F^i = E_F - B$$

Then we can write:

$$\frac{C^{i-v}}{(I_o - C^{i-v})} = z \exp^{-E_F/kT} \exp^{B/kT}$$

where: C^{i-v} is the concentration of single vacancy-single impurity complexes

I_o is the impurity atom concentration

Z is the coordination number

and since

$$C = \text{free vacancy concentration} = \exp^{-E_F/kT}$$

$$\frac{C^{i-v}}{(I_o - C^{i-v})} = Z C \exp^{B/kT}$$

However, this relationship holds only if the number of free vacancies is independent of the number of bound vacancies.⁹⁶ Still further

complications arise since it is not known whether the impurities are dispersed throughout the gold lattice as single atoms or impurity clusters. If the impurities are oversize with respect to the lattice so that strain energy contributes significantly to the binding energy, the misfit of a cluster of these atoms may in effect provide a small dislocation for vacancy precipitation.

One other feature to be noted in the photomicrograph of gold quenched from impure argon at 1000°C is the distinct arrangement of some tetrahedra in pairs (regions marked (A) in Figure 22). Cotterill

attaches considerable significance to the only previous evidence of this pairing which occurred in a gold foil quenched from 750°C and annealed first at 100°C to produce black spots and then re-annealed at 375°C to reveal tetrahedra.⁹¹ Since such pairs had not been reported for quenches closer to the melting point followed by the usual 100°C anneals, Cotterill felt that the paired arrangement was unique to quenching and annealing treatments which involved black spot defects as an intermediate stage. His conception of the origin of these pairs was based on the simultaneous observation that some of the smaller black spots disappeared upon annealing at these higher temperatures while others increased in size. The large spots which subsequently grew to tetrahedra imposed a stress field composed of small regions of compression and tension about each stacking-fault tetrahedra. Free vacancies released by the shrinkage of smaller spots could then migrate to the compressed area around the nearest tetrahedron and thus accelerate the growth of any small spot which may be located there. Other small precipitates which happened to be located in the dilated areas would tend to shrink.

This first photo of tetrahedron pairs produced by quenching from high temperature and directly annealing at 100°C negates the argument that these paired arrangements are peculiar to heat treatments which involve black spot defects as a separate and distinct intermediate stage in tetrahedra evolution. If, however, black spots in gold are in

reality small tetrahedra as indicated previously, then it is perhaps reasonable to expect some discrimination of growth rates among smaller precipitates which happen to lie within the compressed region of larger ones. The low density of tetrahedra due to the removal of some impurity nucleation sites in the case of impure argon might permit some of these favored tetrahedra to grow at an accelerated rate during the growth stage of tetrahedra evolution. The low heterogeneous nucleation rate would allow a greater amount of free excess vacancies to migrate to preferential areas of tetrahedra growth. Conversely, in the instance of dry argon quenches, the high density of heterogeneous nucleation sites would tend to stifle any subsequent paired arrangements during the growth stage. Hence, close examination of Figures 16 and 17 reveals few such tetrahedra pairs for gold quenched from dry argon at 1000°C and annealed at 100°C.

The dilatometer measurements with pure gold also reveal a decrease in the total amount of contraction observed from each quench temperature for single crystals (Figure 10) as compared with polycrystalline wire specimens (Figure 8). Both types of specimens were quenched from a furnace atmosphere of dry argon.

This result at first appears somewhat paradoxical since it would be expected that the grain boundaries in the wires might introduce a greater amount of vacancy loss during quenching than the single crystals.

However, although grain boundaries are indeed very efficient sinks during the quench, the transmission results show that the majority of quenched-in vacancies in gold migrate to vacancy precipitates rather than to the grain boundaries. Since the grain size in the foils was approximately the same as for the wires (about one μm), it is reasonable to expect that the predominant sink in the bulkier dilatometer wire specimens were also vacancy precipitates. However, the as-grown single crystals suffered a greater loss of vacancies at other sinks such as porosity, graphite inclusions, etc., which are found in typical cast structures. The smaller amount of contraction exhibited by the single crystals is a consequence of this vacancy loss during the quench itself or prior to the time of the first dilatometer measurements during the anneal.

The energy of formation of a vacancy in pure gold, E_F , was obtained from the slopes of a semi-logarithmic plot of total $\Delta V/V$ versus the reciprocal of quench temperature (Figure 11). The energy values are tabulated for each type of specimen in Table 3. The gold wires quenched from dry argon yield an energy of formation of 0.71 eV which is somewhat lower than the typical value of 0.98 eV obtained from resistivity measurements and the 0.94 value of Simmons and Balluffi, although it still lies within the theoretical estimates of E_F in gold (0.6 to 0.77 eV).¹⁶ The value of 0.85 eV from the single crystal

measurements is also in agreement with 0.83 ev reported by Pervakov and Khotkevich⁹² and 0.82 ev by Lazarev and Ovcharenko.⁹³ These investigators, however, used gold wires of somewhat lower purity (99.99%). Nonetheless, the resistivity value of 0.98 ev appears to be in good agreement with diffusion data. The activation energy for self-diffusion can be expressed as

$$Q_{S.D.} = E_F^v + E_M^v .$$

Since the energy of migration of single vacancy in gold, E_M^v , was measured by Bauerle and Koehler as 0.82 ev²⁰ and $Q_{S.D.}$ is generally given as 1.81 ev,¹⁸ the sum of E_M^v and E_F^v best fits a value of 0.98 ev for E_F^v . Nonetheless, Koehler has cautioned that experimental errors are generally within the range of 0.1 ev. Gegel⁴⁷ has noted an impurity effect on the migration energy so that future work may possibly alter one or more of these values.

The sources of possible error in the dilatometer technique include vacancy loss prior to the first annealing measurement, temperature fluctuations during anneal and individual specimen variations in purity, grain size, cross-sectional area, etc. Since the reproducibility of three quenches from the same temperature was very good as noted previously in the experimental procedure, it is unlikely that the latter source contributed significantly to the ultimate slope error. The difficulty inherent with the dilatometer technique is the contraction

missed in the first few minutes during insertion of the specimen.

Although the total contraction missed in the gold specimens was small, the variation in insert time from specimen to specimen introduced a further uncertainty in the final volume change.

Alloys

The results of the dilatometer measurements on the gold-silver alloys are shown in Figures 24 to 30 and the deduced vacancy concentration is compiled in Table 3.

The most conspicuous feature of the alloy annealing curves is the marked reduction in $\Delta L/L$ with increasing silver for quench temperatures above 900°C. Thus, while a quench from 1000°C with pure (99.999%) gold wires generated a total volume change ($\Delta V/V$) of 21×10^{-5} , the 80% gold alloy wires exhibited 9.3×10^{-5} and the 60% gold wires produced only 8.6×10^{-5} in volume change. The apparent decrease in vacancy concentration as deduced from the dilatometer measurements of 80% gold wire can be seen by comparison with the pure gold results in Figure 8.

In private communication, J. Takamura has disclosed that his unpublished preliminary data with Au-25%Ag alloys are in agreement with the present results. He likewise has observed a decreased amount of total contraction in the silver alloy for quenches from high temperatures.

The dilatometer runs with pure silver and high silver content alloys were even more striking in contrast to the pure gold since little or no contraction was noted for 21 quench attempts with both polycrystalline wires and single crystals. This result is somewhat surprising since the lattice measurements of Simmons and Balluffi revealed an equilibrium vacancy concentration of 1.7×10^{-4} at the melting point of silver.⁹⁵ Assuming that the fractional volume of a vacancy in the silver lattice is approximately that in gold, then this number of vacant lattice sites should have produced an appreciable amount of contraction (about $9 \times 10^{-5} \Delta V/V$) upon annealing which would have been easily detected by the dilatometer. Nonetheless, the maximum amount of contraction observed at the silver end of the composition range was only $1.05 \times 10^{-5} \Delta V/V$ for a quench from 950°C with a Ag-20%Au wire.

In all other aspects the annealing curves for the alloys quenched from above 900°C are similar to those obtained from the pure gold measurements. A rapid initial contraction was again observed and the final amount of length change decreased with decreasing quench temperatures. This would seem to indicate that the mechanism of vacancy annihilation in the alloy specimens was similar to that of gold. Since the predominant vacancy sink in pure gold was found to be stacking-fault tetrahedra, thin foils of 80%Au and 60%Au were also examined under transmission electron microscopy for similar vacancy precipitates.

Figures 24 to 30. Dilatometer annealing curves for Au-Ag alloy specimens. All alloy compositions are weight per cent (wt. %) and all alloy dilatometer specimens were heated in a dry argon furnace atmosphere.

Figure 31. Total observed volume change versus
reciprocal of quench temperature for
Au-Ag alloy dilatometer samples

The first photograph, Figure 32, is that of an 80% Au alloy foil quenched from 1000°C and aged at room temperature (20°C) for one month. This would thus most closely duplicate the quenching conditions of a dilatometer specimen which was fully annealed and exhibited no further contraction in length (Figure 24).

The room temperature anneal after quenching from 1000°C again reveals the small "black spot" defects less than $100\text{\AA}$ in size similar to those observed in the pure gold foil shown previously in Figure 14. If these spot defects are very small stacking-fault tetrahedra as in the case of pure gold, then the vacancy concentration can be calculated as before from the observed vacancy precipitate density. Indeed, the results in Table 4 show that the vacancy concentration calculated on the basis of tetrahedra density in Figure 14 is in fair agreement with the dilatometer measurement of the same alloy composition. Nevertheless, both the tetrahedra density and dilatometer contraction indicate that the equilibrium vacancy concentration at 1000°C in 80%Au is less than that in pure gold.

If, however, the alloy foil is immediately transferred to boiling water after quenching from 1000°C, the precipitate density and size is increased. The defect structure for both 80%Au and 60% Au alloys annealed at 100°C after quenches from 1000°C is shown in Figures 33 to 37.

Figure 32. Defect structure of an 80wt. %Au - 20%Ag alloy foil quenched from 1000°C into brine and aged at room temperature. The broad, dark curves are bend contours.

(82,000X)

Figure 33. 80%Au quenched from 1000°C and annealed at 100°C. Small black spot tetrahedra are evident rather than the distinct tetrahedra in pure gold produced by the same neat treatment. The short lines are dislocation dipoles or edge dislocations of restricted slip.

(82,000X)

Figure 34. 80%Au; $T_q = 1000^{\circ}\text{C}$; $T_A = 100^{\circ}\text{C}$.

Note the tetrahedra at region marked
(T).

Figure 35. Denuded zone along grain boundary

in 80%Au. $T_q = 1000^{\circ}\text{C}$; $T_A = 100^{\circ}\text{C}$

(60,000X)

Figure 36. Same as Figure 34. Some of the precipitates have triangular shapes at this higher magnification. The dark, straight line running across the photo is not a grain boundary but a micro-crack emanating from an etch pit nearby. The crack was introduced after aging, hence, no denuded zone appears.

(120,000X)

Figure 37. 60%Au foil quenched from 1000°C
and aged at 100°C for one hour
(33,000X)

A denuded grain boundary is shown in Figure 35 and demonstrates that the alloy spot defects exhibit the same behavior on quenching as the vacancy precipitates in gold (Figure 15). Unlike the direct 100°C anneals with pure gold, however, the photomicrographs of these alloys do not reveal large and distinct stacking-fault tetrahedra even at magnifications of 120,000X. Although a few of the spot defects (regions marked T in Figures 34 and 36) do suggest triangular shapes, the majority of precipitates remain unresolvable at about $100\overset{\circ}{\text{\AA}}$ in size. A similar effect was noted in a photomicrograph presented by Smallman at the Argonne Conference in 1964 in which the tetrahedra size in gold was reduced to $100\overset{\circ}{\text{\AA}}$ by the addition of only 0.72%Ag.⁹⁶ Mancini and Rimini also have recently reported black spot defects rather than distinct tetrahedra in gold doped with silver.¹⁰⁸

The defect structure in Figure 38 of pure silver quenched from 900°C and annealed at 20°C consisted of small black spot precipitates less than $75\overset{\circ}{\text{\AA}}$ in size. Although the quality of the silver foils was not good enough to provide a good estimate of the precipitate density, M. Meshii⁹⁷ found the density of black spot defects was on the order of $10^{16}/\text{cm}^3$ for silver quenched under conditions similar to those of Figure 38. (The furnace atmosphere used in Meshii's quenching experiments was not specified, while dry argon was employed for all of the alloy and silver quenches described in the current work.) If the average defect size is estimated at $50\overset{\circ}{\text{\AA}}$, this same density would give a vacancy

Figure 38. Pure (99.999%) silver foil quenched from 900°C and aged at room temperature.

Small black spot precipitates are visible in the background. The large, irregularly shaped images are surface contamination on the foil.

(59,000X)

concentration of approximately 1×10^{-4} which is reasonable. Dislocation loops which had been previously reported in silver by Smallman and Westmacott,⁵⁴ were not observed in the current study nor by Meshii.⁹⁷ Both Clarebrough and Meshii found large, distinct stacking-fault tetrahedra in quenched pure silver and the association of these with black spots suggests that the black spots are very small tetrahedra as in gold.

The transmission results of the alloys and silver show that the predominant vacancy precipitate is the same as that for gold, namely stacking-fault tetrahedra. Furthermore, the density of these defects, especially after 100°C anneals provide for much larger and more reasonable vacancy concentrations than those obtained from the alloy dilatometer measurements. Hence, it appears that a significant amount of contraction must have been lost before the first dilatometer measurements could be made.

Some additional evidence for this pre-anneal vacancy loss in the silver and silver alloys can be found in the resistivity work of Cuddy and Machlin in 1962.²⁹ Upon quenching silver from above 650°C these investigators found that 50% of the excess resistivity had annealed out in less than 10 minutes at an annealing temperature of -18.5°C. Furthermore, significant annealing occurred even at bath temperatures of -34°C!

Clarebrough, et al.³² verified this very rapid annealing rate in silver between -50°C and 10°C and also found that the density of observed

defect clusters was far too low to account for the magnitude of resistance change at these low annealing temperatures. There was general agreement in both papers that this very rapid resistance change was due to divacancy migration to small, invisible, spherical clusters. Doyama and Koehler found that in fact, divacancies are the major point defect retained in silver after quenching from elevated temperatures.⁹⁸

The annealing behavior at low temperatures in silver, then, is quite different from that of gold where no appreciable resistivity changes are evident below -3°C .¹⁶ This difference has been attributed to the relatively large binding energy between two vacancies in silver as compared to gold.¹⁸ The basis for this argument is as follows:

If E_{vv} is the binding energy of two vacancies to form a divacancy and $E_{F(1v)}$ is the formation energy of single vacancy, then $E_{F(2v)}$, the energy required to remove two atoms from the interior of the crystal to the surface becomes

$$E_{F(2v)} = 2 E_{F(1v)} - E_{vv}^B .$$

Also, the concentration of divacancies, excluding entropy terms, may be written:

$$\frac{n_{(2v)}}{N_{\text{sites}}} = C_{(2v)} = 1/2 Z \exp^{-E_F(2v)/kT}$$

where Z = coordination number (12 in fcc)

$C_{(2v)}$ = concentration of divacancies.

Substituting the previous relationship, we find:

$$C_{(2v)} = 1/2 Z \exp^{-2E_F(1v)/kT} \exp^{E_{vv}^B/kT}$$

since

$$C_{(1v)} = \exp^{-E_F(1v)/kT}$$

then

$$\frac{C_{(2v)}}{[C_{(1v)}]^2} = 1/2 Z \exp^{E_{vv}^B/kT}$$

if $Z = 12$ for fcc, then:

$$\frac{C_{(2v)}}{[C_{(1v)}]^2} = 6 \exp^{E_{vv}^B/kT}$$

Hence the equilibrium ratio of divacancies to single vacancies at any temperature, T , is directly dependent on the magnitude of the binding energy between two vacancies.

The other factor to be considered, of course, is the relative mobility in the lattice of the divacancy as compared to a single vacancy. In a face-centered-cubic lattice, an atom which is diffusing by a vacancy

mechanism must pass between four atoms which present a formidable activation barrier. However, the activation energy required for this motion can be effectively decreased by removing one of the barrier atoms to form a divacancy.

The relative importance of the various defects contributing to diffusion at a given temperature depends on their mobility, binding energy and concentration. Unfortunately, at present there are only fragmentary experimental values for the various energy terms required for a complete analysis of the role of vacancies and vacancy complexes in diffusion or quench processes. Table 5 lists some of the current published values for the various energies of vacancies and divacancies in silver and gold. A more complete compilation can be found in sources such as the Argonne Conference volume.¹⁸

A glance at this table shows that the only significant difference in energy parameters between gold and silver apparently lies in the divacancy migration and binding energies. The migration energy, E_{2v}^M , of a divacancy in silver appears to have a firm value of about 0.58 ev while E_{2v}^M of gold is in the range of 0.63 to 0.71 ev. The binding energy of divacancy, E_{vv}^B , in silver is in dispute and the current controversy over E_{vv}^B in gold is even worse. A simmering debate at the Argonne Conference between the Stuttgart group, Seeger, et al, who proposed a maximum of 0.1 ev for E_{vv}^B in gold and the Illinois-Northwestern school who felt it was larger than 0.3 ev, finally prompted

TABLE 5
Properties of Vacancies in Au and Ag

<u>Property</u>	<u>Au</u>	<u>Reference</u>	<u>Ag</u>	<u>Reference</u>
E_{v}^{F}	1.28 (ev)	19	1.10 (ev)	29, 98
	0.98	50, 20	1.049	95
	0.97	35	1.0	45
	0.95	22		
	0.94	15		
	0.83	92, 91		
	0.85	a		
	0.79	21		
	0.71	a		
E_{v}^{M}	0.87 (ev)	93	0.83 (ev)	45, 95
	0.83	50		
	0.82	49		
E_{vv}^{B}	0.3 (ev)	82	0.38 (ev)	98
	0.1	23		
	0.09	34		
$E_{2\text{v}}^{\text{M}}$	0.66 (ev)	23	0.57 (ev)	29, 98
	0.71	82, 25		

^aPresent dilatometer data.

Balluffi to comment that all of the assumptions on divacancies available were just guesses and that what was needed was some experiments which could unequivocally distinguish divacancies by some property peculiar to the divacancy alone.

Even more complications arise since higher vacancy complexes such as tri-vacancies, tetra-vacancies, etc., can be formed in quenched metals. If spherical clusters are formed in silver, as postulated by Machlin and Clarebrough, then free vacancies encountering these clusters will be permanently trapped if the clusters are immobile at low annealing temperatures.

Furthermore, in the alloys the interaction between solute atoms and vacancies must be considered in addition to the binding energy between two vacancies. If the solute-vacancy binding is large, then the divacancy concentration is reduced and the growth of vacancy precipitates will be dependent on the slower migrating single vacancies. A decrease in the growth of precipitates has been noted in Al-Mg alloys where the Mg vacancy binding energy is close to that of E_{VV}^B in aluminum.⁴¹

In spite of these complications and uncertainties in energy values, it does appear that the observed decrease in length contraction in the alloys and silver dilatometer specimens was the result of divacancy migration which occurred in the pre-anneal time before the first dilatometer measurements. The time required to bring the specimens

immersed in the quenching bath at -11°C from the quenching apparatus to the constant temperature room averaged from two to four minutes. Although the vacancies in pure gold were relatively immobile at this low bath temperature, the data of Machlin and Clarebrough shows that in pure silver, significant divacancy migration could occur during this time period even at much lower temperatures.

Additional vacancy loss also occurred in the two to three minutes that were required to insert each specimen in the dilatometer. Therefore, a substantial amount of contraction in the quenched silver and alloy specimens was missed and corrective extrapolation was not satisfactory. This lost contraction diminished the total observed length change and thus decreased the number of obtained data points of total contraction versus quench temperature of these alloys (Figure 31). The quenches from lower temperatures around 900°C approached the limit of instrument measurement and this increased error and the unknown amount of vacancy loss is reflected in the high energy of formation values deduced from the total observed contraction (Table 4).

The formation of spherical clusters in silver as suggested by previous investigators would further tend to diminish the amount of total contraction that was measured. These large clusters would be relatively immobile during the room temperature anneal and thus inhibit the formation of stacking-fault tetrahedra. This would be in accordance with the low density of precipitates shown in the room temperature anneal structure in Figure 32.

The most puzzling phenomena in the 80% and 60% Au alloys is the reappearance of large amounts of contraction for specimens quenched from temperatures below 900°C. The dilatometer annealing curves for these alloy compositions previously shown in Figures 24 to 30 show as decreasing amount of contraction with decreasing quench temperatures until the limit of instrument measurement sensitivity is approached for quenches from around 900°C. If the pre-anneal vacancy loss in these alloys is taken into account, the annealing behavior is the same as that of the pure gold high temperature quenches.

But note in Figure 25 that an 80%Au alloy wires quenched from 600°C produced a volume change of about $10.0 \times 10^{-5} \Delta V/V$, an amount equal to that produced by a quench of the same alloy from 1000°C. This is equal to a deduced vacancy concentration of approximately 1.9×10^{-5} and is in marked contrast to the pure gold quench from 600°C which revealed a mere $0.75 \times 10^{-5} \Delta V/V$ corresponding to a vacancy concentration of 1.4×10^{-7} . The same reappearance was noted in repeated quenches with both 80% and 60% Au alloy wires and single crystals of one mm diameter (Figures 24 to 30). Note in Figure 29 that the 60%Au single crystal exhibited a greater amount of contraction than the same type of specimen quenched from a temperature close to the liquidus line of the phase diagram.

Unlike the previous high-temperature quenches, however, the observed specimen contraction for 80%Au alloys was not directly proportional to the quench temperature, but instead displayed a maximum for quenches from 600°C (Figure 24 vs. Figure 25). A change in length in this alloy was noted for a quench temperature as low as 400°C. This feature was also noted by J. Takamura⁵⁰ who used larger, two mm diameter Au-25%Ag alloy wires. However, when two mm diameter alloy single crystals were substituted for the one mm diameter specimens, no appreciable length change was observed because the larger specimen did not retain the majority of vacancies due to the slower quench rate. A pure gold two mm diameter crystal and a one mm diameter pure silver wire also failed to produce any specimen contraction.

The transmission results of 80%Au alloys quenched from this temperature range are just as interesting. Figures 39 and 40 show the defect structure of an 80%Au alloy foil quenched from 600°C into a brine bath at -11°C and transferred directly to a water bath at 100°C. Even a cursory glance at the alloy structure in Figure 39 as compared with pure gold shown in Figure 19 at a comparable magnification is sufficient to note the marked increase in precipitate density in the alloy though both were quenched from 600°C. The foil thickness, quenching conditions and dry argon furnace atmosphere were the same for the 99.999% gold foil and the 80%Au-20%Ag specimen.

Figure 39. 80%Au foil quenched from 600°C into
brine and aged at 100°C for one hour
(82,000X)

Figure 40. 80%Au. Same as Figure 39.

Precipitates do not resolve to
distinct tetrahedra.

(120,000X)

Figure 41. 80%Au. $T_q = 600^{\circ}\text{C}$; $T_A = 20^{\circ}\text{C}$.

Small spot precipitates at (B).

(60,000X)

Another foil which was quenched from 600°C was allowed to age at room temperature for 72 hours prior to thinning and transmission examination. Black spot defects were again noted (Figure 41) but the small size of the precipitates together with foil surface contamination prevented an estimate of the defect density.

Vacancy concentrations of 80%Au at 600°C calculated on the basis of tetrahedral type sinks in the 100°C anneal structure agree fairly well with the observed dilatometer results (Table 4). Unlike the photographic measurements on the distinct tetrahedra in pure gold, the size of the indistinct spots was difficult to determine, even at magnifications of 120,000X (Figure 40). Nonetheless, the evidence clearly shows that the reappearance of the dilatometer contraction in the alloys after quenching from 600°C corresponds to a marked increase in precipitate density over that observed in pure gold.

There are several possibilities that could account for this phenomena in the alloys, but none appear to satisfactorily explain both the transmission and dilatometer data.

The first explanation, suggested by J. Takamura⁹⁴ on the basis of dilatometry alone, is that some type of ordering occurred in the alloy specimens. Hansen and Anderko⁶⁴ do in fact show a disputed region in the Au-Ag phase diagram located in the vicinity of 50 at. %Au, but the accuracy of the data measurements on the α' phase is in doubt. Therefore, Hansen and Anderko have placed a question mark on the diagram

pending further investigations. If the α' region does exist it still would not account for the substantial increase in vacancy precipitates nor the failure of the two mm diameter alloy crystals to display the same contractions. Since the larger specimens simply were not quenched rapidly enough to retain the majority of vacancies from 600°C, the lack of contraction in these samples implies that the phenomena is associated with the quenched-in vacancies whereas an equilibrium structural change dictated by the phase diagram would be independent of specimen size. Of course, a vacancy induced ordering mechanism rather than an equilibrium phenomenon could also occur. In this case, the reduced amount of vacancy supersaturation in the larger quenched specimen would inhibit the degree of ordering and diminish the amount of observed length contraction.

Another possible explanation of the greater defect density in the alloys quenched from 600°C is that the vacancy concentration is actually higher than that in the pure metal. The effective energy of formation of a vacancy can be decreased by the binding energy to an alloy atom thereby permitting an increase in the equilibrium vacancy concentration.⁹⁹ Such an effect has been noted by Ellwood in Al-Mg alloys.¹⁰⁰

The anomaly between the high temperature quenches and quenches from around 600°C in the same alloy could then be explained on the basis of a change in the role of divacancies in the annealing mechanism. Quenches from higher temperatures lead to a higher concentration of

divacancies than from low temperature quenches for the reason that collisions between the single vacancies occur more frequently with a higher concentration of vacancies. Thus the alloys quenched from elevated temperatures suffered a large amount of vacancy loss in the form of divacancies and higher order clusters. In the quench temperature range of 875 - 925°C, the total vacancy concentration was reduced due to the decrease in quench temperatures, but a substantial portion of this was still in the form of highly mobile divacancies so that little or no contraction was observed. Below these temperatures, however, the vacancy collision frequency is down to the point where divacancy production is low and few single vacancies can escape during the pre-anneal period. The concentration of remaining vacancies is still higher than that of pure gold at the same temperature so that a large amount of contraction is observed during the anneal.

If, on the other hand, the black spot defects produced by the 600°C alloy quenches are quite different than the small stacking-fault tetrahedra in the pure gold structure, then still other possibilities such as solute atom clustering could be considered. However, more information is needed before a final explanation of the alloy specimen behavior could be made. Equilibrium vacancy concentration measurements

of an Au-Ag alloy of the type conducted by Simmons and Balluffi on pure metals would be extremely valuable, as would an investigation of the disputed region in the Au-Ag phase diagram. It would also be interesting to see whether the precipitates could be clearly resolved perhaps by annealing at temperatures higher than 100°C.

Specimen Size Effect

In his original paper on dilatometry measurements of pure gold wires,⁵⁰ J. Takamura presented an experimental relationship between the specimen size and the vacancy concentration.

As before, the general equation for vacancy concentration C is

$$C = A \exp^{(-E_F/kT_q)}.$$

Takamura reported that on the basis of his dilatometer results with one to three mm diameter cylindrical wires the entropy factor A and vacancy formation energy E_F could be expressed as a function of the square of the cylinder radius:

$$A = A_o \exp^{(-ar^2)}$$

and

$$E_F = E_{Fo} - br^2$$

where A_o and E_{Fo} are the values of A and F extrapolated to zero cylinder radius.

Hence:

$$C_T = \frac{A_o}{\exp^{(-ar^2)}} \exp^{-(E_{Fo}-br^2)/kT_q}$$

This would then provide the total amount of vacancies actually quenched into a specimen.

Similar r^2 relationships were derived for the energy of migration of vacancies and also for quenched-in resistivity.

The crux of this r^2 specimen law is that Takamura observed much larger amounts of total contraction with two mm diameter specimens than with the one mm diameter wires. In compliance with these measurements, the br^2 term would decrease the magnitude of the formation energy with increasing radius, r , resulting in higher vacancy concentrations. But the coefficient A also decreases as the specimen radius increases by a factor of $\exp(-ar^2)$ and this should result in a decrease in vacancy concentration. This reduction is, in fact, what would be expected if the cooling rate decreased as specimen size increased since fewer vacancies would be retained during the slower quench.

Takamura could only account for the discrepancy between the observed increase in retained vacancies versus the expected decrease for the 2.0 mm diameter wires by postulating that plastic deformation during quenching generated a large amount of vacancies. Takamura did not advance any mechanism for the production of vacancies by plastic deformation, but felt that somehow more vacancies could be generated through their interaction with dislocations moving under thermal stresses. ¹⁰¹

The amount of vacancies produced by strain was obtained by subtracting the estimated concentration of retained thermal vacancies from the actual total observed vacancy concentration. Takamura

estimated the retained amount of thermal vacancies by experimentally noting that his cooling rate was inversely proportional to the square of specimen radius.

$$C_r = C_o \exp(-ar^2)$$

where C_r = retained thermal vacancies

C_o = actual equilibrium concentration at $r = 0$

Takamura's published result for the difference between this equation and the previous one for C_T is shown in Figure 13. The curves are based on dilatometer gold wires quenched from 850°C and was presented at the Argonne Conference in 1964.¹⁰² The plot shows that as specimen size increases up to two mm diameter, the total volume contraction increases until the total concentration of vacancies in the quenched specimen is higher than the actual equilibrium concentration at 850°C. The retained vacancies would only contribute about 20% to this total while strain generated vacancies represent the majority of vacancies measured.

However, Gegel⁴⁷ and Jackson^{61, 103} have shown that thermal stresses are not an important factor in gold quenched at the normal rates of 10^5 °C/sec. Furthermore, the total volume change represented on the ordinate axis of Figure 13 does not correlate with the observed total volume contraction reported previously by Takamura (Reference 50, Figure 4). Finally, Kimura and Maddin observed that the concentration

of vacancies quenched into undeformed 1.5 mm diameter single crystals was about 40% smaller than the Simmons and Balluffi values. By tension straining some of the crystals at temperature they concluded that the deformed specimens did not show any greater concentration of vacancies than undeformed ones.⁴⁰

In an effort to either duplicate or refute Takamura's observations of increased contraction with increasing specimen size, 2 mm diameter single crystals of random orientation were substituted for the one mm diameter gold ones and a number of quenches were performed from temperatures ranging from 1050°C to 600°C. The experimental conditions, including the average transfer and insert time in the dilatometer, were the same as for the one mm diameter quenches. Nevertheless, no appreciable length changes were observed on annealing during any experimental trial using the larger two mm diameter specimens. Although some contractions less than $10^{-5} \Delta L/L$ were observed, the large amounts of length change reported by Takamura were certainly not seen.

The dilatometer runs were repeated with two mm diameter alloy single crystals ranging from 80%Au-20%Ag to pure silver and quenched from 1000°C to 600°C. Again, little or no contraction was noted.

These results indicate that the larger dilatometer specimens did not retain the majority of vacancies during the quench and that plastic strain did not generate vacancies which would produce a greater

amount of length contraction than observed in the one mm diameter specimens. Takamura himself noted a large deviation from the r^2 law by gold specimens of three mm diameter since this size actually exhibited much less contraction than the one mm size wires. He attributed this deviation to a change in heat transfer in this size of specimen due to the formation of an insulating bubble layer on the wire surface.

The calculations of Gegel and Jackson, coupled with the lack of increased vacancy concentration in the present two mm diameter dilatometer samples and the 1.5 mm crystals of Kimura point to a complete absence of vacancy generation due to quenching strains. Thus, while there is probably some specimen size effect on the retained vacancy concentration, Takamura's composite of curves represented in Figure 13 and the " r^2 " law as a universal relationship do not appear to be justified.

Since some of Takamura's annealing curves show continuing length contraction even after 10,000 minutes of anneal time, this may be a hint of possible specimen deformation perhaps due to an excessive spring load. A similar continuous decrease in specimen length was remedied during the initial dilatometer tests of the present study and discussed in the experimental procedure.

Interaction of Dislocations with Vacancy Precipitates

A fortuitous by-product of the foil preparation for the electron transmission study was the introduction of a few dislocations in the quenched and aged specimens. Although plastic deformation tests of foils have been performed on quenched gold and silver, few photomicrographs of tetrahedra-dislocation interaction in pure gold are available and none of quenched Au-Ag alloys. Since a concurrent hardness study has been undertaken on 80%Au-20%Ag alloys by H. Ike, the photos of this alloy were particularly interesting. It should be stressed, however, that these regions of dislocations represent isolated and infrequent areas in the foils examined and the dislocations did not affect the size and average density of precipitates in the overall structure.

Intuitively, one would expect that a structure which contained a high density of vacancy precipitates such as shown in Figure 18 would inhibit the motion of dislocations in much the same manner as the particles in precipitation and dispersion hardening alloys. The effect of these vacancy precipitates on dislocation motion could then be reflected in tests of mechanical properties such as yield stress, hardness, etc.

Unfortunately, the published results of the effects of quenching gold on mechanical properties are ambiguous, especially for quenches

from lower temperatures.³⁶⁻⁴⁴ Generally, however, there is agreement that individual vacancies, divacancies and small vacancy clusters do not appear to contribute greatly to quench hardening since no hardness of quenched gold is noted until the specimen is allowed to age. There is, of course, some dislocation pinning due to dispersed vacancies which can be measured by internal friction methods, but the increase in yield stress and hardness is small.

After vacancy condensation has advanced to a point in the annealing process where the vacancy precipitate size and density is appreciable, a marked increase in yield stress is noted. Meshii⁸⁹ noted an increase from 400 g/mm² to 1200 g/mm² of the yield stress of gold (99.999%) quenched from 1030°C and aged at room temperature. But specimens quenched and immediately immersed in liquid nitrogen did not display any hardening even after aging for several weeks at -196°C. When these specimens were removed from the liquid nitrogen, hardening took place within 24 hours. A similar increase in yield stress was also noted in quenched silver specimens.

Gegel has reported two separate peaks at 650 and 850°C in a plot of microhardness versus quench temperature for gold quenched into water whereas samples quenched in mineral oil displayed only a continual increase in hardness with increasing quench temperature.⁴⁷ He suggested that these peaks were due to some unknown interaction between

the strain fields of different point configurations. Since the defect configurations in quenched gold are assumed by many authors to be different for quenches above Cotterill's "critical temperature" (stacking-fault tetrahedra) than those from below (black spots), Kimura and Maddin investigated the effect on yield stress of quenching from both temperature extremes.⁴⁴ They found, however, that the hardening characteristics were the same whether the defect structures produced were stacking-fault tetrahedra or unresolvable black spots. Their conclusion was that the black spot defects could be very small tetrahedra.

In this respect the tangled dislocations appearing in Figure 42(a) are interesting, for this combination of room temperature aging and 100°C annealing was known to produce a mixture of both tetrahedra and spot defects (see previous Figure 15). Stacking-fault tetrahedra are in evidence in the regions marked (T) while the smaller spot defects are dispersed throughout the background. Note that at regions marked (B) and (G) both black spots and tetrahedra have effectively pinned the dislocations as evidenced by the cusps along the dislocation lines.

Depending on its Burgers vector, a dislocation moving through the lattice can encounter a repulsive force from each of the tetrahedral arrays of stair-rod dislocations. This is demonstrated at region (ST)

Figure 42a. Pure gold quenched from 1000°C , aged at 20°C for 12 hours and re-annealed at 100°C for two hours. Tetrahedra precipitates at regions marked (T). Dislocation lines are pinned at (B) and (G). Glissile loops are evident at (D) and dislocation dipole at (K).

(52,000X)

Figure 42a. Pure gold quenched from 1000°C , aged at 20°C for 12 hours and re-annealed at 100°C for two hours. Tetrahedra precipitates at regions marked (T). Dislocation lines are pinned at (B) and (G). Glissile loops are evident at (D) and dislocation dipole at (K).

(52,000X)

Figure 42b. Sequence showing moving dislocation line of screw orientation bowing around vacancy precipitates. Note that the Burgers vectors (small arrows) are of opposite sense as two segments of line meet to form loop. In sequence (a), cross over has occurred. In (b), the segments have annihilated to form a glissile dislocation loop. A dislocation dipole and loop are the products in sequence (c).

in Figure 42 (a), where the moving dislocation has encountered a stacking-fault tetrahedron and has begun to bend around the obstacle. Silcox and Hirsch have noted in some instances a distortion of such tetrahedra due to the strain field of the approaching dislocation.⁵²

Since different sections of the dislocation line can move partly independently of each other, the opposite segments of the line can continue around the precipitate, particularly if the line is of near screw orientation. Since the segments are of opposite sign as they encounter each other on the other side of the tetrahedron, they can either (a) cross over on different glideplanes, (b) be annihilated and close off the loop, or (c) even form long parallel segments (in dislocation dipoles). This sequence is sketched in Figure 42 (b) and actually portrays one mechanism of dislocation multiplication within the metal lattice. The three possibilities (a), (b), (c) are shown as the dislocation line moves across three tetrahedra.

Remarkably, all of the configurations sketch in Figure 42 (b) can be found in the actual photomicrograph in Figure 42 (a). Dislocation loops which have been left behind as in the sequence (a) are shown in the regions marked (D) in Figure 42 (a). It should be noted that these are perfect dislocation loops with the conservation of the Burgers vector about the circumference and not the sessile prismatic loops created by the collapse of vacancy disks as discussed previously.

Another dislocation line has crossed over at (F), while a long elongated loop has been left behind at (L). Still another loop at (E) has two parallel line segments at its lip. If two parallel segments like this of opposite sign are separated by a short distance, they can pinch off at both ends to form a dislocation dipole. An example of a dipole can be seen at (K) adjacent to the extended loop at (E).

Other mechanisms of quench hardening which have been forwarded¹⁸ include the formation of jogs by the condensation of vacancies on extended dislocation,^{44, 37} cutting through the stacking-fault tetrahedra,⁴⁴ and the destruction of tetrahedra by dislocation interaction.⁴⁴ There does appear to be a reduction in tetrahedra density in the structure under discussion but verification of precipitate destruction by a moving dislocation would require a sequence of definitive photographs or perhaps a film of a dislocation line encountering a vacancy precipitate.

One other feature to be noted in quenched pure gold is the occurrence of stacking-fault tetrahedra in rows, particularly along $\langle 110 \rangle$ directions. These were first reported by Clarebrough, et al. in 1964 who suggested that they were the result of inadvertent plastic deformation.³² Clarebrough, Corette and Segall¹⁰⁴ also deformed a number of face-centered cubic metals, including gold-tin alloys at room temperature and found stacking-fault tetrahedra in all of

the materials except aluminum and nickel. Consequently, they proposed a model for the formation of tetrahedra involving only glide and cross-slip of dislocations within the condensation of point defects.

Figure 43 illustrates what appears to be such a row of tetrahedra in a gold foil quenched from 1025°C and annealed at 100°C. The entire structure of this same foil consisting of distinct tetrahedra was previously shown in Figure 16. This particular view, however, was obtained from glass plates in a 4 x 5 camera mounted directly on the phosphor screen of the Phillips microscope. Although much higher magnifications could be obtained in this way as compared with the 35 mm camera, very long exposure times were required (about 20 sec) and fluctuations in beam stability impaired the image clarity. Nonetheless, the four tetrahedra are clearly associated with a slip trace (ST) which lies at some angle to the stacking-fault (S) of an extended dislocation. Other tetrahedra are seen at regions (T).

Whether or not the tetrahedra were simply formed by plastic deformation, however, cannot be concluded merely on the basis of photographic association with dislocations. Seidman and Balluffi quenched pure gold, deformed it at room temperature and subsequently annealed the foils at 80°C.⁴² They found rows of tetrahedra but felt that the tetrahedra were not directly formed by moving dislocations but, instead, were heterogeneously nucleated during the subsequent anneal on vacancy debris created during deformation by moving extended

Figure 43. Gold foil $T_q = 1025^\circ\text{C}$; $T_A = 100^\circ\text{C}$.

Note the row of precipitates at (J) apparently associated with slip trace at (ST) and extended dislocation (S). Other tetrahedra are seen at (T).

(170,000X)

jogs, etc. The difference between this conclusion and the direct plastic deformation model proposed by Loretto, et al.¹⁰⁵ would at first appear to be due to the fact that the latter did not quench their specimens to introduce a supersaturation of vacancies. Loretto, Clarebrough and Segall thus ruled out the possibility of point defect contributions. However, this may not be the case at all. In their experimental procedure, these authors merely mention that the foils were prepared in the form of "annealed strip 0.003 inches thick."

The term "annealing" embraces a variety of procedures and since no annealing temperatures or techniques were specified, it is possible that after rolling, the foils were heated to some elevated temperature, removed and air-cooled prior to the actual experimental deformation. In the present study at Ohio State University on Au-Ag alloys, Y. Liu produced a few stacking-fault tetrahedra in some Au-Ag diffusion foils which he had annealed and air-cooled prior to examination. Apparently the thin foils had been air-quenched rapidly enough to retain a sufficient supersaturation of vacancies to form tetrahedral precipitates in the gold. Since the Lorette foils were much thinner than the ones used in the present study prior to thinning, it is conceivable that excess vacancies were also contained in these foils prior to deformation. The fact that Loretto, et al., did not note any tetrahedra in nickel and aluminum could also be explained by the fact that these metals do not

exhibit tetrahedral precipitates even after very rapid quenches.¹⁸ If the Loretto foils were furnace cooled or examined carefully prior to deformation, then no ambiguity would exist. Therefore, further investigations are still needed to completely clarify the role of plastic deformation on tetrahedra formation.

Quench hardening in alloys appears even more complicated than in the pure metals because of the interaction of solute atoms with the excess vacancies. Since the alloys can alter the equilibrium concentration and mobility of vacancies, the type and density of vacancy precipitates may be drastically altered from the pure metal structure and the movement of dislocations may thus be modified.¹⁰⁵

In certain alloys there is also the possibility that excess vacancies can accelerate precipitation of a second phase such as G-P zone formation or enhance an existing order-disorder reaction and thus effect the quench hardness. In the case of the Au-Ag alloys, however, the main effect seems to be a marked reduction in tetrahedra size and an apparent increase in precipitate density. If the pre-existing dislocation density is small then the principal factor in quench hardening the gold alloys would be the effectiveness of these precipitates in impeding dislocation motion.

The photomicrographs of the gold alloys do indicate that the small tetrahedra act as obstacles to moving dislocations even though the precipitates are much smaller than in pure gold.

Figure 44 shows a deformed region between a microcrack (UV) and several overlapping stacking-faults (S) in an 80% Au alloy quenched from 1000°C and annealed at 100°C. As in the case of pure gold, several dislocations are severely bent and pinned by precipitates (B). Glissile loops are again evident at the regions marked (L) although some of the loops in the more tangled regions may have been produced by interacting dislocations rather than from bow-out about a precipitate. The region marked X is shown at higher magnification in Figure 4. Both photos predict that vacancy hardening should be exhibited by an aged 80%Au alloy quenched from this temperature.

Hardness studies currently being performed by H. Ike in Japan do, in fact, tentatively concur with this expectation. The studies were initiated at Ohio State University and the preliminary results of an 80%Au alloy single crystal quenched from 1000°C and annealed at 100°C for one hour show an increase in microhardness over the as-grown condition.

The photomicrographs of 60%Au show similar effects although few dislocations were found during the normal handling of foils. The strength acquired from substitutional solid solution hardening was quite evident in this alloy composition. Very few extended dislocations were found in the foils. The few isolated dislocation lines and dislocations emanating from nearby sources are shown in Figures 45 and 46.

Figure 44a. 80%Au-foil quenched from 1000°C and aged at 100°C. Glissile loops are seen at (L) and small tetrahedra at regions marked T. Kinked dislocation lines and cusps indicating pinning by precipitates are evident in stressed region between microcrack (UV) and several overlapping stacking-faults of extended dislocations at (s).

(63,000X)

Figure 44b. 80% Au foil. Higher magnification view
of region marked (X) in Figure 44a.

(126,000X)

A single dislocation line in this 60%Au alloy foil which was quenched from 1000°C is shown at 82,000X in Figure 45. Bow-out of the line has begun at points (B) and (a) as the line encountered the small vacancy precipitates. The defects are faintly visible in the background (c).

Other dislocations which have been pinned by tetrahedra are shown at (T) in Figure 46. The dislocations at (E) show restricted slip probably because of a near-edge orientation of their Burgers vectors. Another segment of this same slip trace in this 60%Au foil is also shown in Figure 47. A repulsive force is clearly revealed between two dislocation lines at (Z) and a fragmentary network of dislocation lines has started to form at (d). Of course, pure interaction such as this between dislocations contributed to some of the dislocation configurations in the observed microstructures, but the principal strengthening elements are the vacancy precipitates which impede easy dislocation motion.

Unfortunately, no areas of dislocations were found in the alloy foils quenched from 600°C so that a comparison of the strengthening expected from this precipitate structure cannot be made. If the precipitates are stacking-fault tetrahedra as in pure gold, then the quench hardening effect should be approximately the same as that from higher quench temperatures.

Figure 45. 60%Au foil quenched from 1000°C into brine at
-6°C and annealed at 100°C for 45 minutes.
Bow-out of dislocation line around precipitate
has begun at (B).

(82,000X)

Figure 46. 60%Au foil. $T_q = 1000^{\circ}\text{C}$; $T_A = 100^{\circ}\text{C}$.

Note tetrahedra at (T) on dislocation line.

Large dark images are foil surface effects.

(29,000X)

Figure 47. 60%Au. Same foil as Figure 46 showing
apparent interaction between two dis-
locations at (Z) and (D).

(29,000X)

A few quantitative attempts have been initiated to analyze the strengthening mechanism in quenched alloys but the very nature of the precipitates makes an accurate quantitative prediction of such properties as yield stress extremely difficult.¹⁸ The formulas are based on an average precipitate type, size and uniform distribution in the quenched lattice, while in reality all of these factors are quite variable, even at different regions in the same specimen. A great deal of future work is necessary, especially in the alloys.

Etch Pits and Surface Contamination of Foils

Since a great deal of the present knowledge on vacancy behavior in quenched metals rests on the interpretation of electron transmission photographs, it is essential that vacancy precipitates are clearly distinguished from other observed images. Therefore, a brief mention will be made of some effects which, although uncommon in the foils examined, could at first glance be mistaken for vacancy agglomerates.

The first photo in Figure 48 shows a quenched 80%Au foil that contains large and distinct images which bare a remarkable resemblance to the large angular loops reported by Smallman, etc., in Al-Mg alloys.¹⁰⁶ Hexagonal shapes are clearly seen at regions labeled (S) while others appear as dark contrasting dots at (D). In reality, the images were the result of electron beam heating a film of Microstop lacquer which inadvertently remained on the foil after thinning. Subsequent precautions were taken to select foils from the center of the original ribbon where no lacquer had been applied and no loops were ever again noted in any of the foils.

Another surface effect occurred when a thinned alloy foil was re-examined after remaining on copper grid specimen holders for one month. The resulting lamellar structure is shown in Figure 49. The exact origin of this peculiar surface effect is unknown, but the lamellae

Figure 48. 80%Au. $T_q = 600^{\circ}\text{C}$; $T_A = 100^{\circ}\text{C}$.

Hexagonal loops (S) and dark spots

(D) from a film of microstop lacquer.

(42,000X)

Figure 49. Lamellar structure of surface
contamination on 80%Au foil
(61,000X)

Figure 50. 80%Au. $T_q = 600^{\circ}\text{C}$; $T_A = 20^{\circ}\text{C}$.

Crystallographic voids produced by preferential etching during electropolishing of foil. Foil edge is at left of photo.

(29,000X)

Figure 51. 100%Au foil quenched from 600°C
and aged at 100°C. Etch voids of
various shapes and sizes between
two stacking-faults.

(43,000X)

Figure 52. Stacking-fault tetrahedra in pure gold
quenched from 1025°C and aged at 100°C.
(Same foil as in Figure 18.) Note that the
precipitates are visible to the very edge of
the etch voids at the top of photo.

(32,000X)

clearly ran across grain boundaries, etc., and had no crystallographic relation with the metal beneath. This surface contamination was not observed during the original transmission examination of the foil and may be a corrosion product of a galvanic reaction between the copper grid and gold foil. The normal defect structure of small precipitates is still faintly visible in the background of the contaminated foil.

Voids and various crystallographic shapes were also seen in both pure gold and Au-Ag alloy foils. Figure 50 is an example of voids which were found near the edge of an 80% gold specimen quenched from 600°C and aged at room temperature prior to thinning. Other examples in quenched pure gold of voids of various size and shape are shown in Figures 51 and 52.

Yoshida, et al.¹⁰⁷ reported octahedral voids of 25 - 100Å^o in size in aluminum which they felt were directly caused by vacancy clustering to form three-dimensional voids. However, the voids noted in this series of Au-Ag foils do not appear to be a form of vacancy condensation but rather merely crystallographic etching effects. Whereas the Yoshida voids were presumably randomly distributed, the voids in the present study occurred only infrequently and usually were found near the foil edge where preferential etching is expected.

Furthermore, stacking-fault tetrahedra persist to the very edge of the larger voids in Figure 52 without any denuded zone; hence, the voids could not have been formed during the quench.

Vacancy condensation may have indirectly contributed to the formation of voids since preferential attach during the electrolytic thinning operation could conceivably occur at large tetrahedra which intersect the surface, etc. Nevertheless, the voids shown here in Au-Ag do not represent another separate type of vacancy precipitate such as claimed in aluminum by Yoshida.

Summary and Conclusions

The results of the current dilatometry experiments and transmission studies can be briefly summarized as follows:

1. Vacancy concentration in pure gold as deduced from dilatometry length measurements are in good agreement with the equilibrium studies of Simmons and Balluffi, especially for a value of $\alpha = 0.53$.
2. The predominant vacancy sink in pure gold quenched from elevated temperatures and annealed directly at 100°C are stacking-fault tetrahedra. No Frank sessile loops were observed in the quenched structure.
3. Black spot defects appear in the structure of gold quenched from elevated temperatures and subsequently aged at room temperature and, hence, are the principal vacancy annihilation sinks in the dilatometer specimens.

4. These small spot defects grow into large distinct tetrahedra on re-annealing at higher temperatures. This result and the large length change strongly indicate that the spot defects are small unresolvable tetrahedra and not spherical clusters of vacancies.
5. Gold quenched from as low as 600°C still produces vacancy precipitates verifying the predictions of Meshii and Kauffman that stable clusters can be formed at this low quench temperature. The low density of precipitates correlates with the lack of appreciable length contraction at this T_q .
6. Both the fact that Frank sessile loops were not found in the quenched gold structures and the vacancy concentration calculated from precipitate density favor the De Jong-Wilsdorf model of continual tetrahedra growth by annihilation of vacancies at all four faces.
7. Gold wires which were heated in a commercial grade of argon prior to quenching exhibited less total contraction with a decrease in tetrahedra density as compared to similar specimens quenched from dry, ultra-pure argon. This is in agreement with previous reports of the influence of furnace atmosphere on pure gold. The results suggest that impurities which normally act as heterogeneous nucleation sites are removed from the lattice, perhaps by oxidation, although the detailed mechanism is as yet undetermined.

8. Pairs of tetrahedra were also observed for the first time in pure gold after high temperature quenches from a commercial argon atmosphere. Cotterill has suggested that these pairs are formed by preferential growth of one tetrahedra in the compressed region around the other.
9. The as-grown single crystals suffered a greater loss of vacancies at porosity and inclusion sinks during quenching than the polycrystalline wire samples and thus produced a smaller amount of length contraction.
10. The dilatometer annealing curves for the alloy specimens quenched from high temperatures are similar to that of pure gold although a decreasing amount of total contraction was observed as the silver content increased. This is attributed to the loss of vacancies by rapid divacancy migration during the pre-anneal period.
11. The predominant vacancy sinks in the 80% and 60%Au alloy quenched from elevated temperatures again are tetrahedral precipitates, although the precipitate size is drastically reduced from that observed in pure gold.
12. The marked reappearance of length contraction in the alloy dilatometer specimens quenched from temperatures below 600°C is associated with a much higher precipitate density than observed in pure gold quenched from this same temperature range. Although

the exact cause for this substantial increase is not known, it is suggested that the alloys have a higher equilibrium concentration of vacancies and the divacancy migration problem is substantially reduced in the low temperature quenches.

13. Only small black-spot defects were observed in quenched pure silver in agreement with the results of Meshii. No appreciable contraction was found in the dilatometer runs with both wire and single crystal specimens due to divacancy loss prior to the first measurement.
14. The two mm diameter alloy and pure metal dilatometer specimens did not show an increased amount of contraction contrary to the results of Takamura. The present studies, coupled with a similar observation in 1.5 mm gold crystals by Kimura, imply that the " r^2 " specimen size law forwarded by Takamura is not justified.
15. The transmission studies of quenched gold show that both the large distinct stacking-fault tetrahedra and the smaller "black spot" tetrahedra can impede dislocation motion. Glissile dislocation loops and dislocation dipoles were formed by the interaction of moving dislocation lines with vacancy precipitates.
16. The transmission observations of 80% and 60% Au alloys suggest that quench hardening should also be observed in these alloys

when quenched from elevated temperatures. This prediction has been tentatively verified by preliminary hardness data on quenched 80%Au single crystals.

17. Crystallographic voids which were found in quenched Au and Au-Ag alloys are the result of preferential etching effects during electropolishing and do not represent a new form of vacancy precipitation.

REFERENCES

1. Lucretius, "On the Nature of Things" translated by H. A. Munro, Great Books of the Western World, Encyclopedia Britannica, Inc., 1952, p. 20, 5.
2. I. Frenkel, Z. Physik, 35, p. 652, 1926.
3. N. F. Mott & R. W. Gurney, "Electronic Processes in Ionic Crystals," Oxford Univ. Press, 1948.
4. H. B. Huntington and F. Seitz, Phys. Rev., 61, p. 315, 1942.
5. F. R. Nabarro, Rept. Conf. Strength Solids, p. 75, (Physical Society), London, 1948.
6. F. C. Frank, Symp. Plastic Deformation of Crystalline Solids, p. 150 (Carnegie Inst. Technology, Pittsburgh, Pa., 1950).
7. Smigelskas & Kirkendall, Trans. AIME, v. 171, p. 130, 1947.
8. C. Da Silva & R. F. Mehl, Trans. AIME, v 191, p. 155, 1951.
9. L. S. Darken, Trans. AIME, v. 175, p. 184, 1948.
10. W. Seith, Diffusion in Metallen, 2nd. ed., 1955, Springer, Berlin.
11. V. Ruth, Ph.D. thesis (English Translation), Gottingen, 1961.
12. V. Ruth, Trans. AIME, v. 227, p. 778, 1963.
13. H. G. Van Bueren, "Imperfections in Crystals," Interscience Publishers, p. 418, 1961.
14. W. G. Burgers & A. G. Van Zuilichem, Phil. Mag., 7, pp. 981-987, 1962.
15. R. O. Simmons & R. W. Balluffi, Phys. Rev., 125, p. 862, 1962.
16. A. C. Damask & G. J. Dienes, "Point Defects in Metals," Gordon & Breach Publishers, 1963.

17. S. Amelinckx, "Direct Observation of Dislocations," Academic Press, 1964.
18. R. M. J. Cotterill, et. al., "Lattice Defects in Quenched Metals," Academic Press, 1965.
19. J. W. Kauffman & J. S. Koehler, Phys. Rev., 88, p. 149, 1952.
20. J. E. Bauerle & J. S. Koehler, Phys. Rev., 107, p. 1493, 1957.
21. B. G. Lazarev & O. N. Ovcharenko, Dokl, Akad, Nauk., USSR, 100, p. 875, 1955.
22. F. J. Bradshaw & S. Pearson, Phil. Mag., 2, p. 379, 1957.
23. M. De Jong & J. S. Koehler, Phys. Rev., v. 129, pp. 40-61, 1963.
24. D. Jeannotte & E. S. Machlin, Phil. Mag., 8, p. 1835, 1963.
25. J. A. Ytterhus & R. W. Balluffi, Phil. Mag., 11, p. 707, 1965.
26. S. D. Gertsriken & B. F. Slyusar, Fizka Metallov i Metallovedeniye, v. 6, p. 1061, 1958.
27. R. M. J. Cotterill & R. L. Segall, Phil. Mag., 8, p. 1105, 1963.
28. R. L. Segall & L. M. Clarebrough, Phil. Mag., 9, p. 665, 1964.
29. L. J. Cuddy & E. S. Machlin, Phil. Mag., 7, p. 745, 1962.
30. M. Doyama & J. S. Koehler, Phys. Rev., 127, p. 21, 1962.
31. O. N. Ovcharenko, Phys. Metals Metallog., USSR, 11, p. 78, 1961.
32. L. M. Clarebrough et al. Phil. Mag., 9, p. 377, 1964.
33. R. M. Asimov, Phil. Mag., 9, P. 171, 1964.

34. A. Seeger & D. Schumacher, "Lattice Defects in Quenched Metals," Academic Press, pp. 15-74, 1965.
35. W. DeSorbe, Phys. Rev., 117, p. 444, 1960.
36. H. L. Gegel, M.S. Thesis, Ohio State University, 1962.
37. R. Maddin & A. H. Cottrell, Phil. Mag., 46, p. 735, 1955.
38. H. I. Dawson, Acta Met., v. 13, p. 453, 1965.
39. M. H. Loretta, et al., Phil. Mag., 11, p. 459, 1965.
40. H. Kimura & R. Maddin, Acta Met., v. 12, p. 1965, 1964.
41. J. Takamura et al. Journal of the Physical Society of Japan, v. 18, Supplement III, p. 7, 1963.
42. D. N. Seidman & R. W. Balluffi, Phil. Mag., 10, p. 1067, 1964.
43. D. Kuhlmann-Wilsdorf, Appl. Phys. Letters, 1, p. 33. 1962.
44. H. Kimura & R. Maddin, "Lattice Defects in Quenched Metals," pp. 319-386, Academic Press, 1965.
45. S. D. Gertsriken & N. N. Novikov, Fiz. Metal Metalloved, 9, no. 2, p. 224, 1960.
46. S. D. Gertsriken & B. F. Slvusar, Fiz. Metal Metalloved, v. 9, no. 3, p. 465, 1960.
47. H. L. Gegel, Ph.D. Thesis, Ohio State University, 1965.
48. J. R. Cost, Lattice Defects in Quenched Metals, p. 443, Academic Press, 1965.
49. J. E. Bauerle & J. S. Koehler, Phys. Rev., 107, p. 1493, 1957.
50. J. Takamura, Acta Met., v. 9, p. 547, 1961.
51. B. G. Lazarev, et al., Fiz. Metal Metalloved, 7, no. 1, p. 154, 1959 (English Translation).

52. J. Silcox & P. B. Hirsch, Phil. Mag., 4, p. 72, 1959.
53. H. Kimura, et al., Acta Met., 7, p. 145, 1959.
54. R. E. Smallman & K. H. Westmacot, Jnl. of Appl. Phys., 30, p. 603, 1959.
55. G. Thomas & J. Washburn, Rev. of Modern Physics, 35, p. 992, 1963.
56. W. Westdorp, et al., Acta Met., v. 12, p. 495, 1964.
57. T. Mori & M. Meshii, Acta Met., v. 12, p. 104, 1964.
58. J. A. Venables, Phil. Mag., v. 11, p. 1021, 1965.
59. R. L. Segall, Acta Met., v. 12, p. 117, 1964.
60. R. E. Smallman, "Modern Physical Metallurgy," Butterworths, p. 267, 1962.
61. J. J. Jackson, Acta Met., v. 11, p. 1245, 1963.
62. W. D. Lawson & S. Nielsen, "Preparation of Single Crystals," Butterworth Scientific Pub., London, 1958.
63. D. T. J. Hurle, "Mechanism of Growth of Metal Single Crystals from the Melt," Progress in Materials Science, v. 10, no. 2, 1962.
64. M. K. Hansen & K. Anderko, "Constitution of Binary Alloys," McGraw-Hill, 1958.
65. G. Thomas, "Transmission Electron Microscopy of Metals," J. Wiley, 1962.
66. S. D. Gertsriken, N. N. Novikov, & B. F. Slvusar, Fiz. Metal Metalloved, 9, no. 3, pp. 465-467, 1960, English Trans.
67. J. S. Koehler & J. E. Bauerle, Phys. Rev., 1493, v. 6, p. 107, 1957.
68. R. P. Huebener, "Lattice Defects in Quenched Metals," Academic Press, p. 569, 1965.

69. R. P. Huebener & C. G. Homan, Phys. Rev., 129, p. 1162, 1963.
70. R. H. Dickerson, R. C. Lowell & C. T. Tomizuka, Bull. Am. Phys. Soc., v. 9, p. 656, 1964.
71. H. H. Grimes, NASA TN D-2371, July 1964.
72. G. Schottky, A. Seeger & G. Schmid, Phys. Stat. Solidi, v. 4, p. 419, 1964.
73. R. M. J. Cotterill, Phil. Mag., v. 6, p. 1351, 1961.
74. J. S. Koehler & C. Lund, Ref. 18, p. 1.
75. M. Meshii, Ref. 18, p. 412.
76. R. L. Segall, Acta Met., v. 12, p. 117, 1964.
77. B. Chalmers, "Physical Metallurgy," J. Wiley & Sons, p. 332, 1959.
78. N. Thompson, Proc. Phys. Soc., London, 66B, p. 481, 1953.
79. J. P. Hirth, Jnl. of Appl. Phys., v. 32, p. 700, 1961.
80. D. Kuhlmann-Wilsdorf, Acta Met., v. 13, p. 257, 1965.
81. M. Meshii, Ref. 18, p. 402.
82. J. W. Kauffman & M. Meshii, Ref. 18, p. 89.
83. D. Kuhlmann-Wilsdorf, Phil. Mag., v. 11, p. 633, 1965.
84. R. M. J. Cotterill, Ref. 18, p. 109.
85. T. L. Davis & J. P. Hirth, to be published.
86. F. J. Toole & F. M. G. Johnson, J. Phys. Chem., v. 37, p. 331, 1933.
87. W. Eichenaver & D. Liebscher, Z. Naturf., v. 17, p. 355, 1962.

88. J. A. Ytterhus, R. W. Balluffi, J. S. Koehler & R. W. Siegel, Phil. Mag., v. 10, p. 169, 1964.
89. M. Meshii, Ref. 18, p. 387.
90. A. C. Damask & G. J. Dienes, Ref. 16, p. 22.
91. R. M. J. Cotterill, Ref. 18, p. 154.
92. V. A. Pervakov & V. I. Khotkevitch, Soviet Phys. Dokl., v. 5, p. 1051, 1961.
93. B. G. Lazarev & O. N. Ovcharenko, Soviet Phys. - JETP 9, p. 42, 1959.
94. J. Takamura, Private Communication, September 1965.
95. R. O. Simmons & R. W. Balluffi, Phys. Rev., v. 119, p. 600, 1960.
96. R. E. Smallman, Ref. 18, p. 441.
97. M. Meshii, Ref. 18, p. 416.
98. M. Doyama & J. S. Koehler, Phys. Rev., v. 127, p. 21, 1962.
99. W. M. Lomer, Inst. Metals Monograph, v. 23, p. 79, 1958.
100. E. C. Ellwood, J. Inst. Metals, v. 80, p. 605, 1951.
101. J. Takamura, et al., Jnl. of the Phys. Soc. of Japan, supplement III, v. 18, p. 7, 1963.
102. J. Takamura, Ref. 18, p. 547 (Figure 15).
103. J. J. Jackson, Ref. 18, p. 479.
104. M. H. Loretto, L. M. Clarebrough & R. L. Segall, Phil. Mag., v. 11, p. 459, 1965.
105. G. Thomas, Phil. Mag., v. 4, p. 1213, 1959.
106. R. E. Smallman, Ref. 18, p. 591.

107. S. Yoshida, M. Kiritani & Y. Shimomura, Ref. 18, p. 713.
108. S. Mancini & E. Rimini, *Il Nuovo Cimento*, vol. 39, p. 62, September 1965.