QUENCH IN DEFECTS IN SILVER
AND SILVER ALLOYS

by

YUN I. SSU

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
in the Department
of
MINING AND METALLURGY

We accept this thesis as conforming to the
standard required from candidates for the
degree of DOCTOR OF PHILOSOPHY.

____________________________

Members of the Department of
Mining and Metallurgy.

THE UNIVERSITY OF BRITISH COLUMBIA
October, 1960
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FINAL ORAL EXAMINATION

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

of

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QUENCHING IN DEFECTS IN SILVER AND SILVER ALLOYS

ABSTRACT

An investigation has been made of the formation energy, and the activation energy of migration of vacancies in pure silver and its alloys with Cu, Au and Pd. In pure silver the quenched in resistivity rises with increasing quench temperature. In the alloys, however, the quenched in resistivity decreases at first, passes through a minimum and only begins to rise at fairly high quench temperatures. The decrease in the quenched in resistivity in these alloys may be attributed to the destruction of short range order existing in the well annealed specimens. This mechanism is similar to that invoked by both Damask and Korevaar in similar experiments. The annealing characteristics of these quenched specimens also confirm this view. A method, other than that used by Korevaar, for evaluating the formation energy, of a vacancy was used. The results so obtained yield values for $E_f$ of 0.8 ev and $E_m$ ranging from 70 ev to 1.02 ev. These results seem reasonable, although it is felt they are insufficiently accurate and extensive to warrant detailed conclusions concerning the effects of specific alloying elements.

GRADUATE STUDIES

Field of Study: Physical Metallurgy

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<tr>
<td>Solid State Physics</td>
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<td>Nuclear Engineering</td>
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PUBLICATIONS


ABSTRACT

An investigation has been made of the formation energy, and the activation energy of migration of vacancies in pure silver and its alloys with Cu, Au and Pd. In pure silver the quenched in resistivity rises with increasing quench temperature. In the alloys, however, the quenched in resistivity decreases at first, passes through a minimum and only begins to rise at fairly high quench temperatures. The decrease in the quenched in resistivity in these alloys may be attributed to the destruction of short range order existing in the well annealed specimens. This mechanism is similar to that invoked by both Damask and Korevaar in similar experiments. The annealing characteristics of these quenched specimens also confirm this view. A method, other than that used by Korevaar, for evaluating the formation energy, of a vacancy was used. The results so obtained yield values for $E_f$ of 0.8 ev and $E_m$ ranging from .70 ev to 1.02 ev. These results seem reasonable, although it is felt they are insufficiently accurate and extensive to warrant detailed conclusions concerning the effects of specific alloying elements.
The author is indebted to Dr. V. Griffiths for his supervision of the work carried out till 1959 and to Dr. E. Teghtsoonian for his supervision thereafter. He is grateful to Professor R.E. Burgess and Mrs. A.M. Armstrong for their preliminary reading and comments on various parts of the manuscript. He also wishes to thank Mr. R. Butters and Mr. R. Richter for their technical advice and assistance, also Mr. W. Irvine, Mr. K.G. Davis and Mr. S. Saimoto for their critical discussions and untiring help in the preparation of the thesis. He also wishes to acknowledge the cooperation of the Mines Branch of the Department of Mines and Technical Surveys through whose courtesy the vernier potentiometer was obtained on loan.

The work was financed by the Defence Research Board of Canada under Grant Number 7510-33, and by the National Research Council.
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AND SILVER ALLOYS

INTRODUCTION

In the past ten years there has been a number of experiments based on quenching and annealing techniques to evaluate the activation energy of diffusion in metals. Gold and platinum being highly resistant towards oxidation were often used in these investigations. Results obtained for these metals agree with those obtained by self-diffusion experiments. Silver is a noble metal whose properties have been well studied, yet so far as we are aware, no quench experiments on it have been reported.

Moreover, as is generally known, small additions of foreign substances affect the diffusion rate markedly. A few experiments have been performed on alloys of low concentration (less than 1%) by quenching and annealing techniques. One experiment with an exceptionally high alloying content is that on a 7 atomic percent Cu in Au alloy. There has been no attempt as yet to investigate the effect of a particular alloying element on the energy of formation and migration of a vacancy.

It is deemed useful if the formation energy and the activation energy of migration of a vacancy in silver can be obtained by these methods. It is also interesting to ascertain if similar methods can be applied to silver alloys. From the results of these experiments it might be possible to probe further the effect of the alloying element on the formation energy as well as on the activation energy of migration of a vacancy in these alloys. It is in view of these considerations that the present investigation was undertaken.
I. Theoretical Review

1. Formation of vacancies.

Vacancies are formed at elevated temperatures by thermal excitation and reached an equilibrium concentration given by an equation of the form
\[ c = A \exp\left(-\frac{E_f}{RT}\right) \]
where \( E_f \) is the formation energy of a vacancy, i.e., the energy required to extract an atom from the interior of the metal and place it on the surface of that metal, and \( A \) is the frequency factor. The theoretical calculation of this energy for copper has been carried out by Huntington and Seitz\(^1\) and by Huntington.\(^2,3\) Huntington arrived at a value for the formation energy of a vacancy in copper of 1.5 to 1.8 ev.\(^4\) Once a vacancy is formed it may move through the lattice by a process of position exchange with nearest neighbour atoms. Before and after the exchange the atom is in a stable position where the potential energy is a minimum. It requires a certain amount of energy to surmount the potential barrier between these equilibrium positions and this energy, \( E_m \), is referred to as the activation energy of migration. Huntington also gave the activation energy of migration as 0.9 ev. The sum of these two energies is in reasonable agreement with the experimentally measured activation energy of self diffusion in copper, namely 1.92 ev, measured by Kuper et al.\(^5\) The frequency with which such exchanges occur can be expressed by an exponential function \( B \exp\left(-\frac{E_m}{RT}\right) \). The profound effect of the temperature upon this frequency is obvious. Taking \( E_m = 0.5 \) ev, the ratio of the rate at 600°K to that at 300°K is about \( 4.5 \times 10^4 \), i.e., if the jumping frequency is one per second at 600°K it will be one in \( 4.5 \times 10^4 \) seconds, i.e., about one in twelve hours at 300°K.
2. **Evidences for vacancies**

Visual evidence for the existence of vacancies is not readily obtained since they are voids of atomic size. Their existence can, however, hardly be disputed. Vacancies are considered to account for the magnitude of self diffusion in metals and, more convincingly, for the Kirkendall effect with its accompanying porosities. It is also generally observed that the density of a quenched metal is lower than that of a slowly cooled metal although no visible holes are present. Tiny voids which are clusters of vacancies have actually been observed using small angle X-ray scattering techniques.\(^6\),\(^7\)

However, quantitative measurements concerning vacancies are in general made not by any of these means, but rather by their effect on some physical property such as hardness or electrical resistivity.

3. **Relative effect of vacancies and other defects on electrical resistivity.**

The electrical resistance of a metal arises from distortion of the perfect periodicity of the ideal lattice. Disregarding the thermo-vibrational component of resistivity and considering only the residual component, point defects such as vacancies exert a large influence and are several orders of magnitude more effective than line or planar defects such as dislocations, grain boundaries or surfaces. From the point of view of measuring the contribution of vacancies to electrical resistivity this difference is very important and makes quench experiments useful.

Thus, for instance, when a wire of finite size is quenched from a high temperature to \(0^\circ\text{C}\) and immediately plunged into liquid nitrogen in order to freeze-in the vacancies, thermal stresses may be created between the outer and inner parts of the wire, and may generate dislocations and stacking faults.
The effect of these imperfections on electrical resistivity is usually relatively small in comparison with that due to frozen-in vacancies.

Another complication arises from the formation of divacancies and vacancy clusters in close packed metals. This process has been investigated by Bartlett and Dienes\(^9\) and by Kierstadt.\(^\text{10}\) Some evidences of such phenomena is inferred from Bauerle and Koehler's\(^\text{11}\) work on the annealing of quenched pure gold wire.

Theoretical calculations of the electrical resistivity associated with vacancies have been made by various authors: Dexter,\(^\text{12}\) Jongenburger,\(^\text{13}\) Abeles,\(^\text{14}\) Blatt,\(^\text{15}\) and by Stehle and Seeger.\(^\text{16}\) Various expressions for the potential fields arising from vacancies have been assumed by these authors, but the predicted effects on electrical resistivity are generally in agreement. Dexter's value of the resistivity increment per atomic percent of vacancies was lower (0.4 \(\mu\Omega\)-cm) than those for the other investigators which ranged from 1.25 to 1.67 \(\mu\Omega\)-cm.

The electrical resistivity resulting from scattering due to divacancies in monovalent metal has been calculated by Bross and Seeger.\(^\text{17}\) Provided there is no preferred orientation of the divacancies the residual resistivity decreases by 10% upon the association of single vacancies to form divacancies. It is also interesting to note that in their investigation, deviations from Matthiessen's law were negligible. The electrical resistivity resulting from scattering of electrons at a cluster of vacancies has been calculated by Dexter.\(^\text{18}\) His results, because spherical cavities were assumed, were more applicable to larger clusters. He found that as the clusters increase in size the stored energy associated with the cluster decreases while the ratio of resistivity/ stored energy of the defects increases. Some of his results are cited.
The effect of the presence of edge dislocations on electrical resistivity has been investigated by Kohler, Mackenzie and Sondheimer, Landauer and Dexter and that of screw dislocations by Hunter and Nabarro. An edge dislocation was considered by Landauer as a line dipole whose strength may be calculated from the elastic displacements about the dislocation line. On the other hand, Koehler and Mackenzie and Sondheimer obtained scattering potentials from the ionic displacements about the dislocation line. All authors agreed that the scattering potential associated with edge dislocations varies slowly. Since there is no dilatation associated with screw dislocations their contribution to the electrical resistivity is thought to be even smaller. Hunter and Nabarro and Seeger and Stehle had calculated the scattering of electrons from screw dislocations. The results given for copper by various authors are listed below; and it may be noted that the electrical resistivities due to dislocations are anisotropic.

### Table 1

<table>
<thead>
<tr>
<th>Vacancy cluster formed by n vacancies</th>
<th>1</th>
<th>10</th>
<th>100</th>
<th>1000</th>
<th>10000</th>
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<tr>
<td>Resistivity $\mu\Omega\cdot\text{cm per At. percent}$</td>
<td>2.22</td>
<td>1.35</td>
<td>0.686</td>
<td>0.343</td>
<td>0.168</td>
</tr>
<tr>
<td>Resistivity per unit stored energy density $\Omega\cdot\text{cm/ev/cc.}$</td>
<td>.</td>
<td>.</td>
<td>.</td>
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### Table 2

<table>
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<tr>
<th>Type of dislocation</th>
<th>Direction of Current</th>
<th>$\Delta\rho \mu\Omega\cdot\text{cm} \times 10^{-20}$ for random orientation</th>
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<tr>
<td>Edge dislocation</td>
<td>$\perp$ slip plane $\perp$ in slip plane dislocation</td>
<td>1.37 0.64</td>
</tr>
<tr>
<td></td>
<td>$\perp$ slip plane $\parallel$ in slip plane dislocation</td>
<td>0.44 0.6</td>
</tr>
<tr>
<td>Screw dislocation</td>
<td>$\perp$ slip plane $\perp$ in slip plane dislocation</td>
<td>0.26 0.17</td>
</tr>
<tr>
<td></td>
<td>$\perp$ slip plane $\parallel$ in slip plane dislocation</td>
<td>0.26 0</td>
</tr>
<tr>
<td></td>
<td>$\parallel$ slip plane $\parallel$ in slip plane dislocation</td>
<td>0.26 0</td>
</tr>
<tr>
<td></td>
<td>$\parallel$ slip plane $\perp$ in slip plane dislocation</td>
<td>0.17 0</td>
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<tr>
<td></td>
<td>$\parallel$ slip plane $\parallel$ in slip plane dislocation</td>
<td>0.17 0</td>
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<tr>
<td></td>
<td>$\perp$ slip plane $\parallel$ in slip plane dislocation</td>
<td>0.17 0</td>
</tr>
<tr>
<td></td>
<td>$\parallel$ slip plane $\perp$ in slip plane dislocation</td>
<td>0.17 0</td>
</tr>
</tbody>
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Blatt, Ham and Koehler\textsuperscript{24} have investigated theoretically the effect of stacking faults on electrical resistivity and have found the effect in copper and silver to be small. They gave the following values:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Copper</th>
<th>Silver</th>
<th>Gold</th>
</tr>
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<tr>
<td>$\Delta \rho \Omega \text{-cm} \times 10^{20}$ (unit density of S.F.)</td>
<td>0.021</td>
<td>0.056</td>
<td>1.55</td>
</tr>
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These results are not undisputed. Most experimental results dealing with the change of electrical resistivity associated with plastic deformation are higher than the values derived from theoretical calculations. There have been two suggestions to explain this discrepancy. On the one hand, Dexter\textsuperscript{18} has suggested that vacancies or vacancy clusters generated by plastic deformation could be responsible for a large part of the resistivity increase associated with plastic deformation; on the other hand, Broom\textsuperscript{25} and Koehler\textsuperscript{26} suggested that the stacking faults themselves could be responsible for the discrepancy. There is experimental evidence to support the latter view. Christian and Spreadborough\textsuperscript{27} found in their experiments that stacking faults contribute significantly to the electrical resistivity of a deformed metal.
II. Previous Work on Quench Experiments

One of the quench experiments was reported by Bauerle and Koehler. They found the energy of formation $E_F$ of a vacancy in gold to be 0.98 ev. This value is a little smaller than Kauffman's which is 1.28 ev with pre-cooled helium gas as the quenching agent instead of water. Specimens quenched from various temperatures and annealed in the neighbourhood of 40°C were found to possess activation energies of migration of vacancies $E_m$ which depended on the quenching temperature, being smaller for higher temperatures, e.g.,

<table>
<thead>
<tr>
<th>Quench temperature</th>
<th>700°C</th>
<th>800°C</th>
<th>900°C</th>
<th>1000°C</th>
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<td>Activation energy of migration ev.</td>
<td>0.82</td>
<td>0.66</td>
<td>0.63</td>
<td>0.60</td>
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The explanation offered to account for this effect was that some divacancies, whose $E_m$ is smaller were formed very early during the annealing treatment and that the higher the original quenching temperature the greater the number of divacancies that were formed. It was found that the annealing kinetics for the specimen quenched from 700°C was practically exponential and the quenched-in resistivity could be annealed out completely at room temperature in about 150 hours, while the quenched-in resistivity for higher quench temperatures decayed in a more complicated way and about 10 percent persisted even after prolonged room temperature annealing. The measured $E_F + E_m$ is in good agreement with the recent self-diffusion measurements of Okkerse.

Similar investigations concerning platinum have been carried out by several workers. Bradshaw and Pearson determined the formation energy of a vacancy in platinum and its corresponding activation energy of migration to be 1.4 and 1.1 respectively. Ascoli et al. obtained slightly different values: the formation energy of a vacancy was found to be 1.19 ev with air quenching and 1.23 ev with water quenching. Their annealing experiments were
carried out at seven temperatures ranging from 453°C to 578°C. They calculated the activation energy of migration from the half time of resistivity decay to be 1.42 ev. The measured $E_f + E_m$ agreed with the results of similar experiments performed by Lazarev and Ovcharenko, namely, 2.6 ev, and with activation energy for self diffusion of Kidson and Ross who obtained a value of 2.9 ev.

Similar experiments have also been performed on aluminum, e.g.

Bradshaw and Pearson

\[ E_f = 0.76 \text{ ev} \quad E_m = 0.44 \text{ ev} \]

Panseri et al

\[ E_f = 0.74 \text{ ev} \quad E_m = 0.25 \text{ ev} \]

DeSorbo and Turnbull

\[ E_f = 0.79 \text{ ev} \quad E_m = 0.52 \text{ ev} \]

For the last example, the measured $E_f + E_m$ (1.31 ev) corroborates that (1.4 ev) obtained by Spokas using nuclear magnetic resonance measurements, and also agrees with the theoretical estimate (1.43 ev) of Norwick.

The good agreement between the results of these numerous experiments indicates that current interpretations of the process are essentially correct.

III. Measurements and Results

1. Preparation of specimens

A twenty-gram sample of 99.9995 purity silver (Johnson and Mattey) was melted in an alundum crucible in open air and cast in a quartz tube by suction action. The ingots were cold drawn to 0.0143 inch diameter wires, which were subsequently grain-stabilized at 900°C for four hours and cooled slowly in the furnace. The wires were given a further annealing treatment for one week in a water bath held at 60°C. 20 cms lengths of wire were cut and employed in the experiments. Potential leads also made of pure silver wire, 0.002 inch in diameter, were spot welded onto each of the specimen at positions of about 7 to 8 cms from the ends. This left a length of the useful
middle section of the specimen of about 5 cms. Two of these units were now mounted on a rectangular silver frame.

2. Quench experiments.

a. Procedure:

The method of measuring quenched in resistivity was that devised by Koehler and Bauerle. The assembly consisted of a specimen and a dummy wire of the same material and geometrical dimensions. The arrangement is shown in Figure 1. A standard resistor $R_1$ was inserted to measure the current. When the variable resistance is so adjusted that the galvanometer shows no deflection the following condition applies:

\[ I_s = I_d = \frac{1}{2} I \]

\[ r_d I_d - r_s I_s = V_{12} \]

\[ (r_d + r_d)I_d - (r_s + r_s)I_s = V_{34} \]

it follows that

\[ r_s - r_d = \frac{V_{12} - V_{34}}{I_s} = \Delta r \]

Matthiessen's rule states that resistances are composed of two additive parts, one due to impurities $r_i$ (in the present case, vacancies and dislocations) and the other due to thermal scattering $r_T$. The latter contribution in one arm cancelled that in the other arm. Thus:

\[ r_s - r_d = (r_{si} + r_{siT}) - (r_{di} + r_{diT}) = r_{si} - r_{di} = \Delta r_i \]

where the subscripts $s$ and $d$ denote specimen and dummy respectively.

The heating and quenching processes were carried out in a lucite vessel, partially filled with a saturated brine solution whose temperature
Figure 1(a). Balanced Circuit

Figure 1(b). Series Circuit

Figure 1(c). Layout of Apparatus
was maintained in the range -4°C to -8°C. The specimen assembly was mounted horizontally about 0.5 cm to 1 cm above the water surface by a spring clamp. Selected temperatures were achieved by allowing an appropriate amount of direct current from a lead storage battery to pass through the specimen arm for at least ten minutes to ensure establishment of equilibrium vacancy concentrations. During this heating period the potential drop across the specimen and the current through it were measured with a potentiometer. The resistivity of the specimen at this heating temperature was then calculated and the temperature inferred from the known resistivity versus temperature calibration curve of pure silver (Fig. 2). The specimen was then quenched by dropping the assembly into the brine solution by releasing the clamp, immediately after which the heating current was shut off. The assembly was then transferred as quickly as possible into a liquid air tank made of styrofoam. Subsequent measurements were made therein.

Measurement of the temperature of the hot specimen was troublesome, because, due to the large temperature gradient between the hot specimen and the ice water, steady state conditions were not realized and the temperature of the specimen fluctuated within limits of about ±10°C. For a given heating current the temperature of the specimen depended critically on its separation from the water surface. Nevertheless the results indicated a reasonably definite and fairly reproducible increase in resistivity.

The uniformity of heating temperature along the specimen was checked at high temperatures with an optical pyrometer but this check could not be applied at lower temperatures. The uniformity of heating at the lower temperature range was simply assumed since the non-uniformity of temperature was mainly due to the conduction of heat through leads to the frame and conduction loss was presumably less for the smaller temperature gradient.
Fig. 2 Resistivity versus Temperature

Pure Silver
Present investigation, purity 99.9995%
Handbook Am. Inst. Phys. purity 99.98%
The speed with which the specimen was transferred into the liquid air after quenching was important, especially for pure silver specimens. If, by some accident, this process had been delayed, subsequent measurements showed smaller quenched-in resistivity. The necessity for the second rapid quench can be understood with reference to the annealing experiments conducted by Cooper et al. in connection with effects on resistivity of irradiation defects. According to their findings, the vacancies in irradiated silver begin to anneal out at about 200°C whereas the corresponding temperature for pure gold is about 240°C. Hence for silver a fast quench rate and rapid transfer is essential.

Initially, a Leeds and Northrup K-2 potentiometer, which was capable of detecting directly 0.5 μm was used. Later, a Vernier potentiometer manufactured by Cambridge Instrument Co. and accurate to 0.1 μm was obtained. The measuring current was necessarily limited to 50 ma or less, since otherwise, a steady current could not be maintained. This situation was improved but not eliminated completely by continuously charging the battery with another battery. The cause of the changing current seemed due not only to the changing e.m.f. of the battery, but also to thermal e.m.f. along the circuit, or other factors. At these necessarily small currents the balanced circuit method of Koehler, because the voltages $V_{12}$ and $V_{34}$ were small, did not permit an accuracy of measurement in excess of three or four figures, and the last figure was, in general, not definite. Furthermore, it was found that the balance condition shifted slightly during the course of measurements. Therefore, the balanced circuit method was abandoned and some points of the quench curve were obtained by using a current of less than 0.05 amp through a series arrangement consisting of the specimen, the dummy and the standard resistance, and measuring individually the potential drops across them. All
these measurements were carried out twice with reversed e.m.f.'s. The galvanometer leads were also occasionally reversed to check parasitic e.m.f.'s. The quenched-in resistivities measured with the balanced circuit were consistent with those measured with a series circuit as is shown on the same plot (Figure 3).

b. Results and accuracy:

The formation energy, $E_f$, of a vacancy in pure silver was evaluated statistically from the slope of the $\ln \Delta \rho$ versus $1/T$ curve (Figure 4), by assuming the relationships

$$\Delta \rho \propto n_v \propto n \exp(-\frac{E_f}{kT})$$

where $\Delta \rho$ is quenched in resistivity, $n_v$ is the number of quenched in vacancies, $n$ is the number of atomic sites and $T$ is the temperature from which the specimen was quenched. The $E_f$ so determined was 0.82 ev. The statistical error was no more than 0.02 ev. However, the uncertainty in quench temperature is not included in the error given above. The instant at which quenching was carried out was selected so that the potential drop across the specimen and the current, as measured from the potential drop across the standard resistance, did not fluctuate too rapidly (as observed from the deflection of the galvanometer). It is nevertheless difficult to estimate accurately the effect of fluctuating voltages since $V$ and $I$ were not measured simultaneously. These were measured alternately and each entry was the result of three to five such measurements. Also the amount of cooling which occurred during the interval between releasing the specimen and the actual quench was unknown. All these factors made the knowledge of quench temperature relatively uncertain. Since the quench temperature effects the defect resistivity greatly, the error in $E_f$ may have been fairly large. An accurate overall estimate of these errors is difficult to make but it is believed to be less than 0.1 or 0.2 ev corresponding to an
Quenched in Resistivity ohm-cm.x10^9

Figure 3. Quench Experiments of Pure Silver.
Quenched in Resistivity ohm-cm x 10^9

\[ \frac{1}{T} \times 10^4 \text{ cm}^{-1} \]

Figure 4. ln versus \( \frac{1}{T} \); Pure Silver

\( E_p = 0.82 \text{ ev.} \)
uncertainty in the quench temperature of about 10°C at 1000°K. This approximate error is estimated in the following way:

\[ \Delta \rho = A \exp \left( -\frac{E_f}{kT} \right) \]

\[ \frac{E_f}{k} = \frac{\ln \Delta \rho - \ln \Delta \rho_i}{\frac{1}{T_1} - \frac{1}{T_2}} \]

\[ E_f = | \frac{\partial E_f}{\partial \Delta \rho_i} d \Delta \rho_i | + | \frac{\partial E_f}{\partial T_1} dT_1 | + | \frac{\partial E_f}{\partial T_2} dT_2 | \]

from the quench experiments it is found that at \( T = 800^\circ K \), \( \Delta T = 10^\circ C \) and \( \Delta \rho = 320 \times 10^{-10} \text{ ohm-cm} \),

\[ d \Delta \rho = 40 \times 10^{-10} \text{ ohm-cm}. \]

while at \( T = 1000^\circ K \), \( \Delta T = 10^\circ C \) and \( \Delta \rho_2 = 2600 \times 10^{-10} \text{ ohm-cm} \),

\[ d \Delta \rho_2 = 600 \times 10^{-10} \text{ ohm-cm}. \]

By substitution, \( \Delta E_f = 0.2 \text{ ev.} \)

In the light of the quench rate measurements ( Appendix 1 ) it appears likely that the actual quenched in vacancy concentration was smaller than the equilibrium value at the quench temperature. The initial air cooling could have decreased the vacancy concentration to a lower value. It is probable that quenches from high temperatures involved the loss of more vacancies than quenches from lower temperatures and thus a smaller formation energy was found.
3. Annealing Experiments

It was first thought possible to determine the formation energy of a vacancy from the initial annealing rates of specimens quenched from two high temperatures but annealed at the same temperature, and the activation energy of migration from the half-time of the annealing curves or from the annealing rates obtained at two successive annealing temperatures for specimens quenched from the same high temperature. However, the methods involving initial rates were unsuccessful.

a. General features of annealing curves:

After the quenched in resistivity measurements had been made, some quenched specimens were annealed in a constant temperature water bath at selected temperatures between 20°C and 50°C accurately controlled to 0.1°C. The resistivity dropped very rapidly during the first half minute and subsequently the rate decreased. Some of these annealing curves are shown in Figure 5. Although the numerical values of the annealing rate depended on quench temperature as well as on annealing temperature, the general shapes of these curves are characteristically alike.

The technical difficulties encountered in evaluating the initial rate of annealing were mainly due to the fact that the defects annealed very fast even at room temperature. It was so fast that no curve composed of closely linked points could be obtained and therefore the precise slope of the curve was difficult to establish. This difficulty arose from several factors. First of all, both the specimen assembly and the annealing medium have finite heat capacities. When the assembly was brought into the annealing vessel the temperature of the latter, as indicated on a thermometer located close to the specimen, showed a drastic decrease and recovered its initial value only after a few minutes. Therefore the actual temperature for short time
(a) quenched from 691°C, annealed at 18.9°C
(b) quenched from 693°C, annealed at 29.2°C
(c) quenched from 642°C, annealed at 29.2°C

Figure 5. Initial Rate of Annealing; Pure Silver
annealing was not precisely known. Secondly, the specimen assembly had to be transferred from the liquid air tank to the annealing vessel for annealing and then brought back to the liquid air tank for measurement. Each transference took a second or two and inasmuch as the specimens were at temperatures above 200°C during these intervals it is possible that the defects annealed. Thirdly, the quench temperature and also the corresponding quenched in resistivity were not exactly reproducible for each particular point (although it is quite reproducible for the entire curve) since the quenching conditions could not be accurately controlled.

There were also difficulties associated with the complex nature of the quenched in defects themselves. The fact that the annealing curves for high temperature quenches were not exponential, (e.g. Figure 6) might indicate that the defects were not single vacancies alone but rather a combination of single vacancies, divacancies, vacancy-clusters and/or dislocations.

b. Annealing behaviour of the specimens quenched from high temperature:

According to Bauerle and Koehler's results concerning the annealing behaviour of gold wires quenched from 800°C and 900°C, the decay of the defect resistivity was slow at first, then increased continuously (for 900°C quench) or broke suddenly to a much faster rate (for 800°C quench) and then decreased slowly again to some asymptotic value which was larger for higher quench temperatures. The initial annealing rate was consistent with the rate observed for quenches from 700°C. The decay curve of the specimen quenched from 700°C was exponential and the measured activation energy of migration (0.82 ev) was attributed to single vacancies. The activation energy of migration of the defects at the latter part of the annealing curve for specimens quenched from 800°C and above was smaller (0.65 ev) and was
(a) quenched from 691°C, annealed at 18.9°C
(b) quenched from 693°C, annealed at 29.2°C
(c) quenched from 642°C, annealed at 29.2°C

Figure 6. Initial Rate of Annealing; Pure Silver
attributed to a combination of single vacancies and divacancies. After prolonged annealing, as much as 10 percent of the defect resistivity remained depending on the purity of the specimen used. This analysis is very helpful for understanding the present experiments. The annealing curves for pure silver specimens may be divided into three stages with respect to time; stage (1), less than a minute, stage (2), from one minute to one hour, stage (3), upwards of one hour.

Stage (1): There was no portion of the curve for pure silver which corresponded to the part associated with slower initial annealing rates as in pure gold. However, on closer examination this difference is related only to the appearance of the graph and does not indicate a difference in the physical process involved. It has been shown previously that a vacancy in pure silver begins to move at 200°C, which is about 40 °C below the corresponding point for pure gold. Single vacancies, in a fraction of a second after the specimen is placed in the annealing bath, might very well move to and combine with nearby vacancies to form divacancies or vacancy-clusters or might disappear at a suitable sink before any measurements have been made. Thus, changes in the initial annealing rate of the curve may not have been detected. Once the vacancies combine into divacancies and vacancy-clusters the defects concentration is reduced drastically and, moreover, since the divacancies and vacancy-clusters scatter electrons less effectively than single vacancies the quenched in resistivity decreases sharply.

To change the annealing temperature at this early stage was found to be impractical in view of the rapidly changing slopes involved, and as mentioned before, the precise shape of the curve was not established. No activation energy of migration of the defects at this stage could be calculated.
Stage (2): The activation energy of migration for the defects as calculated from the data shown in Figure 7 is 0.67 ev. This is considered to be the activation energy of migration of complex defects, a combination of single vacancies and divacancies.

Stage (3): Often, the differences between the annealing rates at various temperatures near room temperature were too small to be measured accurately. The remaining quenched in resistivity was as high as 30 percent of its initial value. If Kauffman and Koehler's interpretation is adopted, the remaining resistivity would have to be considered as due to impurities. Oxygen pick-up during the heating period was considered. The presence of impurities should make necessary corrections for the formation energy as well as for the migration energy. However, the uncorrected $E_f$ was close to the expected value, and, furthermore, it was found that the quenched in resistivity obtained by quenching a virgin specimen from a low temperature could be reproduced within the possible scattering even after that specimen had been heated at a high temperature. This might indicate that oxidation was not a serious factor.

In the present investigation the measured quenched in resistivity resulting from a quench from 1000°K was about $300 \times 10^{-10}$ ohm-cm. A severely cold worked specimen may have a dislocation density of the order of $10^{12}$ dislocations per cm$^2$, and, according to Hunter and Nabarro's calculation, a unit density of edge dislocation would give rise to an electrical resistivity of $1.37 \times 10^{-20}$ ohm-cm for a current running in a direction normal to the slip plane and $0.44 \times 10^{-20}$ ohm-cm if it is parallel to the slip plane. Thus for a severely cold worked specimen the contribution to the electrical resistivity due to dislocations is about $1.37 \times 10^{-20} \times 10^{12} = 137 \times 10^{-10}$ ohm-cm, that is $137/300 = 46\%$ of the initial quenched in resistivity. Since dislocations are not expected to anneal readily at room temperatures this amount of the elec-
Figure 7. Annealing Experiments of Pure Silver.
cal resistivity would have remained for a long time. Alternatively, stage (3) of the annealing curve may also be explained by a process involving dissociation of the vacancy-clusters formed at the beginning of the annealing process. Dissociation would have increased the number of scattering centers but the single vacancies formed would undergo annihilation at sinks leading to an approximately constant concentration of defects. Since the number of vacancy clusters did not change rapidly in these processes, the net effect on the resistivity would have been small and the rate of annealing would have been very slow.

c. Annealing behaviour of the specimens quenched from 580°C.

Occasionally specimens heated up to less than 600°C and quenched would give exponential decay curves and most of the quenched in resistivity could be removed by room temperature annealing. Figure 8 is an example; only the first point deviates from the exponential expression. This deviation accords with the assumption that the initial rapid decrease in resistivity was due to the formation of divacancies. The activation energy of migration was evaluated by assuming \( \frac{dn}{dt} = n \exp\left(-\frac{E_m}{kT}\right) \) and \( n \gg \Delta n \), so that \( \frac{d \ln \Delta \rho}{dT} = A \exp\left(-\frac{E_m}{kT}\right) \). The value obtained by successive anneals at two different temperatures was in this case 0.79 ev. This value is a little larger than that obtained with specimens quenched from high temperatures. Therefore, this higher activation energy of migration may be attributed to single vacancy, the sum of the formation energy of a vacancy and its activation energy of migration in silver is thus 1.61 ev, which is again in fair agreement with the activation energy of self diffusion in silver. A list of the self diffusion activation energy for silver reported by various investigators is given below.
<table>
<thead>
<tr>
<th>Authors</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Johnson</td>
<td>2.00</td>
</tr>
<tr>
<td>Hoffman and Turnbull</td>
<td>2.00</td>
</tr>
<tr>
<td>Slifkin, Lazarus, Tomizuka and Tomizuka</td>
<td>1.98</td>
</tr>
<tr>
<td>Slifkin, Lazarus and Tomizuka</td>
<td>1.90</td>
</tr>
<tr>
<td>Nachtrieb, Petit and Wehrenberg</td>
<td>1.90</td>
</tr>
<tr>
<td>Johnson and Martin</td>
<td>1.77</td>
</tr>
<tr>
<td>Krueger and Hersher</td>
<td>1.95</td>
</tr>
<tr>
<td>Kryukov and Zhukovitski</td>
<td>2.06</td>
</tr>
<tr>
<td>Finkelstein and Yamashchikova</td>
<td>1.96</td>
</tr>
<tr>
<td>Zhukovitski and Geodakyan</td>
<td>1.96</td>
</tr>
<tr>
<td>Kucsynski</td>
<td>1.83</td>
</tr>
<tr>
<td>Tomizuka and Sonder</td>
<td>1.92</td>
</tr>
</tbody>
</table>
Figure 8. Annealing Experiments of Pure Silver

Specimen quenched from 570°C

$E_m = 0.79$ ev.
PART II - SILVER ALLOYS

I. 2 Atomic Percent Cu in Ag.

1. Preparation of specimens.

0.2400 grams of high purity copper and 19.7616 grams of 99.9995 percent purity silver were melted in a sealed quartz tube filled with nitrogen gas at a pressure of 1/3 atmosphere. The melt was constantly stirred for some time and cooled in the tube. Subsequently the alloy, being relatively less subject to oxygen attack, was remelted in an open crucible with nitrogen gas blowing gently over the surface of the melt. When the melt became clear it was cast in a quartz tube by suction action. The ingots were slightly cold-worked and homogenized in a nitrogen atmosphere at 764°C for six days. These samples were then drawn down to 0.0145 inch diameter wire and subsequently annealed and furnace cooled. Specimen and dummy lengths were cut and mounted on the frame with 0.002 inch silver wire as potential leads.

2. Quench experiments

As for pure silver the general experiments were made in open air. The horizontally mounted specimen, being positioned about one cm or less above the pre-cooled brine solution (about -5°C), was heated electrically and quenched. The resistivities were measured in a liquid nitrogen tank, and the following results were obtained:

<table>
<thead>
<tr>
<th>Heating current (amp)</th>
<th>0</th>
<th>8.47</th>
<th>9.75</th>
<th>10.45</th>
<th>10.72</th>
<th>11.60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quenched in resistivity ($\times 10^{-9}$ ohm-cm)</td>
<td>0.22,42</td>
<td>27.74</td>
<td>37.51</td>
<td>47.72</td>
<td>53.71</td>
<td></td>
</tr>
</tbody>
</table>

For these results, approximate temperatures were estimated from the calibration curve of the 2 At. percent Au in Ag alloy (Figure 9) and were
Fig. 9 Resistivity versus Temperature.

2 At. Percent Au in Ag Alloy
believed to be in the range 400°C to 800°C in ascending order with the heating currents.

3. Negative quenched in resistivity

The observed negative quenched in resistivity was first interpreted as due to the result of diffusion of copper atoms to the surface where they were oxidized thereby reducing the copper content of the matrix and resulting in decreased resistivity. In view of the more rapid diffusion of vacancies in silver alloys compared with pure silver, it would have been desirable to quench and transfer the specimen to the liquid air vessel for measurements even faster than for the pure silver experiments. However, it was difficult to design a method whereby the heating, quenching, and transferring processes could all be made without bringing the specimen into contact with the air. Moreover, it would have been impossible to provide for air-tight sealing of the 0.002 inch leads with the protective envelope. Therefore, the experiments with 2 At. percent copper alloys were abandoned.

II. 2 Atomic Percent Au in Ag.

1. Preparation of specimens.

In order to avoid the adverse effects of oxidation, specimens containing 2 At. percent Au in Ag were made to replace the Cu-Ag alloy. 0.7233 grams of high purity gold and 19.2767 grams of 99.995 percent silver were melted together in open air. The ingots were slightly cold-worked and homogenized in a nitrogen atmosphere at 784°C for nine days. They were drawn into .013 inch wire. The possibility of recrystallization and grain growth effects during the actual experiments were eliminated by first annealing the wire samples at 750°C for one hour and subsequently at 900°C for more than two hours and finally cooling slowly in the furnace. The crystals could be seen
with the unaided eye, and were, on the average, about 0.1 mm diameter. This grain structure remained stable during the course of the experiments.

2. **Negative quenched in resistivity**

The quench experiments were conducted by the same method that had been used for pure silver and negative quenched in resistivities were again observed. These experiments were repeated on three specimens, two of which had been subjected to the same heat treatment described above. The third specimen was annealed, grain stabilized and then ordered by heating it with a twelve ampere current for one half hour and subsequently reducing the heating current one ampere every five to ten minutes. When the current was reduced to three amperes it was shut off. The existence of a negative quenched in resistivity was established conclusively but the quench curve seemed to depend in some way on the previous heat treatment of the specimen. The result for the first two specimens is given in Figure 10.

As a result of this experiment oxidation of a component of the alloy was ruled out as the sole cause of the negative quenched in resistivity. Gold is more oxidation-resistant than silver and if the silver component in the alloy had been at fault the effect of oxidation of silver would also have shown up in the pure silver experiment. However, as this effect had been negligible with pure silver, an alternative explanation was sought.

3. Damask's experiment and explanation.

Damask had measured the electrical resistivity of Cu₃Au after quenches from various temperatures above the critical temperature for long range order. He determined that the resistivity measured at 77°K decreases with increasing quench temperature up to 485°C. Above 496°C the quenched in resistivity increased with the quenching temperature. At liquid helium
Figure 10. Quench Experiments; 2 At. % Au in Ag Alloy
temperatures (4°K) a similar behaviour was observed which differed only in that the slope of the quench curve at 4°K was about 2 percent steeper than that at liquid air temperature. It was accordingly surmised that the effect of short range ordering on the thermal contribution of resistivity up to 77°K was small. The origin of the resistivity decrease was assigned to the destruction of short range order in the alloy.

4. Korevaar's experiment and explanation.

Similar experiments had also been carried out by Korevaar on a 7 At. percent Cu in Au alloy, quenched from temperatures in the range 60° to 900°C. The quenched in resistivity measured at 77°K rose slightly for quenching temperatures from 60°C to 200°C but dropped steeply at approximately 200°C. The curve levelled off thereafter and increased gradually from 500°C upward. The same explanation as that above, i.e., based on short range ordering was advanced to explain these results. From the initial rates of ordering during annealing after quenching from 900°C and from 450°C, the energy of formation of a vacancy was estimated to be 0.93 ev. The activation energy of migration of a vacancy in this alloy was determined to be 0.60 ev. The sum of these values is in reasonable agreement with estimates of the activation energy for self diffusion.

5. X-ray evidence of short range order in gold-silver alloy.

The literature was surveyed for X-ray evidence of short range order in gold-silver alloys. Norman and Warren using X-ray techniques had found considerable short range order at 300°C in the alloy containing 25 At. percent Au. The results indicated about 9.45 silver atoms were associated with the first coordination shell of a gold atom as compared with the random value of 9. The critical ordering temperature computed from these results by Cowley's theory is 160°K which is so low that long range order could not possibly be
established at a reasonable rate.

6. Aarts and Jarvis' experiments.

Aarts and Jarvis\textsuperscript{43} found that the resistivity of Au-Ag alloy wire specimens decreased suddenly with stretching at liquid air temperatures and an increase in resistivity occurred when the deformed alloy was annealed at room temperature. These results were explained by assuming that elastic strain at the low temperature increased the degree of order and that heating to room temperature produced disordering which remained on cooling again to the liquid air temperature. However, it is considered that these results are better interpreted using Korevaar's explanation.

7. Evaluation of $E_f$.

Single vacancies might undergo any or all of the following three processes:

(1) A single vacancy might combine with another to form a divacancy. The rate of this process would be proportional to $n^2$ where $n$ is the concentration of single vacancies. By reducing the number and power of scattering centres, this process decreases the resistivity.

(2) A single vacancy might diffuse to and be removed at sinks. The effect of this process is also to decrease the resistivity and the rate of decrease is proportional to the concentration of single vacancies, i.e., $n$.

(3) A single vacancy might interact with a gold atom to produce short range ordering, effect of which is to increase the resistivity. The rate of decrease due to this process is proportional to the product of concentration of the single vacancies and that of gold atoms in the alloy.
The resultant effect on resistivity of these processes can be expressed by the following equation

\[ \frac{d\Delta \rho}{dT} = -C_1 n^2 - C_2 n + C_3 n \]

where the C's are constants for a particular composition. Thus, unless the formation of divacancies was negligible, the initial resistivity change during annealing would not be proportional to the concentration of single vacancies. This was found to apply to pure silver and possibly also to 2 At. percent Au in Ag alloys. Hence, Korevaar's method for estimating the formation energy of a vacancy in silver alloys from the initial rates of annealing of specimens quenched from two different temperatures cannot be considered a suitable one for this alloy. There are also practical difficulties inherent in Korevaar's method. First, the initial annealing rate depends on the quench temperature used which, however, as mentioned before, could not be controlled precisely. Second, since \( E_f \) is determined from the annealing rates for any two quenches, the statistical assembly would be small unless a large number of annealing experiments were carried out. Third, graphical measurement of the slopes is generally inaccurate especially for the rapidly changing initial part of the annealing curve.

If it is assumed, first, that at the temperature corresponding to the minimum of the quench curve, short range ordering was small and, secondly, that the tendency for a decrease in the electrical resistivity due to the destruction of short range order is compensated for by an increased tendency for resistivity change due to the quenched in vacancies, then the increase in resistivity in the latter part of the quench curve at high temperatures would be due solely to the latter cause. The original vacancy equation may be manipulated in the following manner: differentiating \( n \propto \Delta \rho = A e^{\frac{-E_f}{KT}} \) and
assuming that $E_f$ is practically constant in the temperature range of interest:

$$\frac{d\Delta \rho}{dT} = A \frac{E_f}{K T^2} e^{-\frac{E_f}{K T}}$$

i.e.,

$$B T^2 \frac{d\Delta \rho}{dT} = e^{-\frac{E_f}{K T}}$$

where $A$ and $B$ are constants and $\frac{d\Delta \rho}{dT}$ can be found from the quench curve for each temperature. From the slope of a secondary plot of $\ln \frac{T^2}{dT} \frac{d\Delta \rho}{dT}$ versus $\frac{1}{T}$, Figure 11, the formation energy of a vacancy, $E_f$, is determined. The $E_f$ thus obtained for the 2 At. percent Au in Ag alloy is only 0.47 ev, a value too small to be reasonable. A possible explanation was found in later experiments on a 25 At. percent Au in Ag alloy for which the short range order corresponding to a fully ordered Ag$_3$Au structure was found to persist beyond 850°K. For the present alloy (2 At. percent Au in Ag) the minimum of the quench curve occurred at 560°K; thus, in the temperature range from 560°K to 850°K it is likely that the measured increase in resistivity which was attributed solely to quenched in vacancies was actually less than the true value by an amount due to destruction of short range order.

8. **Annealing experiments**

In the present study, several annealing experiments were carried out and the typical results for one of them is shown in Figure 12. The annealing curves were similar to those of pure silver; no rise of the electrical resistivity was observed. The dissimilarity between the annealing curves for this dilute Au-Ag alloy with those for the Cu-Au alloy studied by Korevaar might be explained by two factors:

1. At the low concentration of gold involved, it is possible that a large number of vacancies combined with each other into divacancies or
Figure 11. \( \ln(T^2 \frac{d\rho}{dT}) \) versus \( \frac{1}{T} \times 10^4 \) K\(^{-1} \); 2 At. Percent Au in Ag Alloy.
Figure 12. Annealing Experiments; 2 At. Percent Au in Ag Alloy

Specimen quenched from ~950°C

$E_m = 0.66 \text{ ev.}$

Annealing Time Hrs.

Annealing Experiments; 2 At. Percent Au in Ag Alloy

Resistivity ohm-cm x 10^9

36.7°C

55.3°C

12 days' annealing
vacancy clusters, or diffused to some sinks before they encountered gold atoms so that no apparent ordering was observed.

(2) The ordering effect on electrical resistivity in the 2 At. percent Au in Ag alloy was probably much smaller than that in the 7 At. percent Cu in Au alloy. Therefore, although both alloys contained only small amounts of the addition, the ordering effect was more pronounced in the Cu-Au alloy than in the Au-Ag alloy.

As in the case of pure silver, it was impractical to change the annealing temperature at an earlier time. At the later times the increase in resistivity, due to short range ordering, partly cancelled the decrease in resistivity due to removal of vacancies. The net rate of annealing was so small that accurate measurements were not obtained. \( \Delta_m \) estimated from Figure 12 was 0.66 ev.

In order to study this effect more thoroughly it was decided to perform experiments on Au-Ag alloys of high gold concentration.

III. 25 At. Percent Au in Ag.

1. Preparation of specimens.

According to Norman and Warren there are two ordered states for gold silver alloys at the compositions corresponding to AuAg and AuAg\(_3\). A AuAg\(_3\) alloy was prepared by melting 7.5433 grams of gold in 19.9241 grams of silver in an alundum crucible in open air and casting the melt into a quartz tube as before. The ingots were slightly cold-worked and homogenized in a helium atmosphere at about 900°C for seven days. After homogenization one ingot was drawn down to wire 0.013 inch in diameter. This wire was grain stabilized and order in a helium atmosphere by heating to a temperature of 900°C and
gradually cooled down at a rate of about 30°C per hour to 700°C and 10°C per hour to 200°C and about 5°C per hour to room temperature. The cooling was arrested and the temperature held overnight at each of 700°C, 300°C, 200°C, 120°C and 50°C, after which the wire was taken out of the furnace.

2. Quench experiments

The quenches were conducted in the usual manner, i.e., in the pre-cooled brine solution. The results of a set of quench experiments are shown in Figure 13. Different specimens of the same alloy gave similar quench curves; these did not always coincide very well at low quench temperatures but fitted quite closely at high quench temperatures where the vacancy effect was more prominent than the ordering effect.

If, as before, the quantities of $\frac{\Delta \rho}{dT}$ were calculated from the quench curve and plotted on a semilogarithmic scale against $\frac{1}{T}$ (Figure 14), a straight line was obtained. The slope was comparatively less than that of the graph of $\ln \Delta \rho$ versus $\frac{1}{T}$ of pure silver and thus a smaller formation energy of a vacancy, namely, 0.75 ev. resulted.

The method used to derive $E_f$ from the initial rates of increasing resistivity was not successful. Reasons given for the case of 2 At. percent Au in Ag alloy can also be applied here. One example is shown in Figure 15. The $E_f$ obtained this way was smaller than the one given above.

3. Annealing experiments

The specimen was heated up once more to some point above the temperature at which the quenched in resistivity versus quench temperature curve showed a minimum. After the quenched in resistivity was measured, the specimen was annealed isothermally at 19.4°C (±0.1°C) for five or ten seconds several times and the residual quenched in resistivities at liquid nitrogen temperature
Figure 13. Quench Experiments of 25 At. Percent Au in Ag Alloy
Figure 14. $\ln(T^2 \frac{d\Delta P}{dT})$ versus $\frac{1}{T}$; 25 At. Percent Au in Ag Alloy.
(a) quenched from 1208°K, annealed at 19.4°C
(b) quenched from 1030°K, annealed at 19.4°C
(c) quenched from 1010°K, annealed at 38.1°C
(d) quenched from 990°K, annealed at 38.1°C

Figure 15. Annealing Experiments of 25 At. Percent Au in Ag Alloy Specimens, Quenched from two High Temperatures
were measured each time. This process was repeated at 33.6 (± 0.1°C) and then again at 19.4°C. During these experiments the bath temperature was changed only when the annealing curve had attained a stable form such that it seemed possible to predict its future course. These results are shown in Figure 16. The activation energy of vacancy migration in this alloy was about 0.70 ev.

The extra resistivity over its initial value before quench was considered to be the contribution of the residual vacancies. Measurements on this specimen were not continued further but it is believed that additional annealing would eventually have reduced the quenched in resistivity to zero. This prediction was verified in the experiments on Pd in Ag alloys described below.

The resistivity versus temperature calibration was carried out in the same way as for pure silver and the calibration curve is shown in Figure 17.

IV. 25 At. Percent Pd in Ag.

1. Preparation of specimens.

The alloy was made by melting 4.5896 grams of sponge palladium and 13.9219 grams of 99.9995 percent purity silver in an alundum crucible in open air and casting the melt in quartz tubes. These specimens were remelted and cast to improve homogeneity. The final ingots were slightly cold worked and homogenized at 950°C for six days. They were drawn into wires of approximately 0.013 inches in diameter. These wires were grain stabilized at 640°C for 12 hours and finally subjected to an ordering treatment by holding at 950°C for 12 hours and subsequently cooling slowly at a rate of 15°C per hour to
Specimen quenched from 1208°K. $E_m = 0.70$ ev.

Figure 16. Annealing Experiments; 25 At. Percent Au in Ag Alloy
Fig. 17 Resistivity versus Temperature

25 At. Percent Au in Ag Alloy
520°C. They were held there overnight and cooled further at a rate of 10° to 5°C per hour to room temperature.

2. Quench experiments.

The quench experiments were conducted as described previously. A negative quenched in resistivity was again observed, the minimum of which was located about 100°C above that of the 25 At. percent Au in Ag alloy. At a quench temperature above 950°K the quenched in resistivity began to rise. As the quench temperature was increased beyond ~1200°K, the 0.002 inch silver wire serving as potential leads became very weak and often broke during the quench (on three specimens). So the experiment was repeated using as potential leads thin wire of 0.002" x 0.004" dimension made from an alloy of the same composition as that of the specimen. With these potential leads, the quench temperature could be raised to 1350°K. The quench curve is shown in Figure 18.

The resemblance of the quench curve for this alloy and that of the 25 At. percent Au in Ag suggested strongly the existence of short range order in the Pd-Ag alloy. Direct measurements of the short range order of this alloy could not be found in available literature. But none of the information about this alloy or of similar alloy systems such as Pd-Cu contradicted the short range order assumption.44 This alloy system had been extensively studied in the early 1930's. The system exhibits a continuous range of solid solution over the whole composition range and no superlattice had been observed.45 Since ideal solid solutions rarely occur and there was no long range order, any local deviation from homogeneity in this case may have led to the formation of some sort of short range order. The Pd-Cu alloy of similar composition44 was known to exhibit an ordered state at temperatures below 600°C. When a quenched specimen was annealed, an initial increase in resistivity was observed for all alloys of compositions 6 to 30 percent of Pd. The initial increase in resistivity...
Figure 18. Quench Experiments of 25 At. Percent Pd in Ag Alloy

(a) $E_f = 0.77 \text{ ev.}$

(b) $E_f = 1.66 \text{ ev.}$
vity during annealing was attributed to the nucleation process of the ordered phase. The authors proposed that, "in any nucleation process, the nuclei are initial smaller in linear dimensions than the mean free path of the conduction electrons. Thus one would expect the nuclei to behave as additional scattering centers and increase the resistivity. As the number of nuclei increases, the resistivity will increase until the nuclei have grown to a size such that the mean linear dimensions are larger than the appropriate mean free path. Then since the resistivity of the ordered material is lower than that of the disordered material, further growth of the domains will cause the resistivity to decrease. However, the 6.4 At. percent Pd-Cu alloy did not show ordering at annealing temperature 400 to 450°C. It may be argued in view of the superlattice lines not being observed in this region, that the above reasoning would also apply if the rise in resistivity were due to an increase in short range order." The above quotation is used here only to assert the fact that short range order in the Pd-Cu alloy increases the resistivity. The idea that the linear dimensions in comparison with the appropriate mean free path serve as a criterion for the resistivity to increase or decrease is not necessarily endorsed. In fact, Damask had found that the resistivity of a brass decreased with increasing short range order.

Recent experiments conducted by Aarts and Houston-Mcmillan substantiated the result of the present investigation. They observed in a 25 At. percent Pd in Ag alloy a decrease in resistivity with 10% extension and suggested that an increase in the number of conduction electrons due to the distortion of the Brillouin zone as a result of plastic deformation is responsible for the change. However, in the present quench experiments the specimen was so thin that plastic deformation could not have been appreciable and consequently the author is inclined to accept the short range order explanation.

On close examination, the quench curve of the 25 At. percent Pd in Ag
alloy seems to be composed of three sections. After passing the minimum, the quenched in resistivity increases sharply till about 1100°K is reached. From 1100°K to the neighbourhood of 1200°K the increase of resistivity becomes slower and from 1200°K up it increases steeply again. These features were observed in three specimens, two of which gave enough points for plotting a quench curve before the specimens were destroyed by some cause such as breakage of potential leads etc. The formation energy of a vacancy calculated from the slope of a secondary plot of $\frac{\tau^2 d\rho}{dT}$ versus $\frac{1}{T}$ (Figure 19) is about 1.6 ev for the high temperature section of the quench curve and is 0.77 ev for the low temperature section. It is still not known why there should be a step in the quench curve. If this step is considered accidental or false and is ignored and the vacancy resistivity is counted from the minimum, the formation energy of a vacancy calculated from the slope of this vacancy resistivity versus $\frac{1}{T}$ in semilogarithmic plot is then about 0.88 ev.

3. Annealing experiments

The specimen was heated up to 937°C and quenched and its quenched in resistivity measured. It was subsequently annealed at 95°C (± 1 or 2°C) six times and continuously at 107°C (± 1 or 2°C) five times. The results are shown in Figure 20. The resistivity continuously increased but with successively smaller increments due to the decrease in the available vacancy concentration. When the annealing temperature was raised the electrical resistivity rose at a higher rate for a while by virtue of higher mobility of the vacancies at that temperature; then it levelled off and reached a maximum at which the rate of increase in resistivity due to the effect of the short range ordering was presumably balanced by the decrease in resistivity due to the loss of the vacancies to various sinks, such as grain boundaries and surfaces. Passing this maximum, the electrical resistivity decreased slowly. Further annealing
Figure 19. $\ln\left(\frac{T^2 \Delta \rho}{dT}\right)$ versus $\frac{1}{T}$; 25 At. Percent Pd in Ag Alloy
Figure 20. Annealing Experiments; 25 At. Percent Pd in Ag Alloy.
at 250°C (±2°C) for several hours reduced the resistivity to a level close to its initial value before quenches. Therefore in this specimen the annealing process followed even more closely the pattern developed by the 7 At. percent Cu-Ag alloy in Korevaar's experiments. It also seemed to justify the assumption that oxidation of the silver component did not contribute significantly to the increase and decrease of the electrical resistivity of the specimen.

The activation energy of migration of a vacancy in this alloy is 1.02 ev. The temperature versus resistivity calibration was carried out in open air and the result is shown in Figure 21.

**SUMMARY**

In Part 1 the various theoretical treatments of the problem were reviewed and the use of electrical resistivity measurements as a means of investigation were discussed. Previous work concerning quench experiments, and the experiments and results of the present work with pure silver were described and discussed. The formation energy and the activation energy of migration of a vacancy in pure silver were found to be 0.82 ev and 0.79 ev respectively.

Part 2 was devoted to silver alloys (2 At. percent Cu in Ag, 2 At. percent in Ag, 25 At. percent Au in Ag and 25 At. percent Pd in Ag). The quenching and annealing characteristics of silver alloys were very different from those of the pure metal. Damask's experiment and his suggested explanation, also Korevaar's experiment were described. The effect of short range order on electrical resistivity of these alloys was considered to explain the differences between the quenching and annealing behaviour of pure silver and that of its alloys. An alternative method to evaluate the formation energy of a vacancy in these alloys was applied and it was found that the energy of
Fig. 21 Resistivity versus Temperature

25 At. Percent Pd in Ag Alloy
formation of a vacancy in pure silver was slightly greater than that in silver alloys. This was in agreement with the expected contribution of the local strain energy. From the similarity of the quenching and annealing behaviour of the 25 At. percent Pd in Ag alloy and that of the corresponding Au in Ag alloy, one is naturally led to assume the existence of short range order in the former. From an assessment of the accuracy of the experimental results, it seems reasonable to plot the results of the Pd-Ag alloy (Figure 18) as a double branched curve. However, there has been no adequate explanation for this feature. The activation energy of migration of a vacancy in the Pd-Ag alloy was found to be greater than that in the Au-Ag alloy and in pure silver. This activation energy arises from the work required for a migrating atom to surmount the potential barrier exerted by neighbouring atoms. Since the repulsive force here is of a short range nature, the activation energy of migration would be affected more than the formation energy. This was predicted by Lazarus.48
BIBLIOGRAPHY

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Measurements of Quench Rates.

The quench rate was measured with a Tetronix oscilloscope. Figure 22a is a photograph of the pattern obtained when a silver specimen was quenched from 400°C into a brine solution maintained at a temperature of about -4°C.

The vertical scale on the oscilloscope was adjusted to 50 millivolts per unit length and the horizontal scale to 10 milliseconds per unit length. The specimen was kept in a horizontal position less than 1 cm. above the quench solution.

The initial portion of the curve which exhibited a slower cooling rate corresponded to the air quench before the specimen entered the quench solution. The second portion of the curve represents the true water quench. The bottom line indicates the zero potential level after the heating current was turned off. Fig. 22b is a similar photograph for a silver specimen quenched from 580°C, other conditions being the same. The vertical scale
in this case was set at 100 millivolts per unit length and time scale was the same as before. Both pictures give the average quench rate 10°C per millisecond approximately.

In the light of the above measurements it appears quite likely that the actual quenched in vacancy concentration was smaller than the equilibrium value at the supposed quench temperature. The initial air cooling could have decreased the vacancy concentration to a lower value. It is probable that quenches from high temperatures involved the loss of more vacancies than quenches from lower temperatures and thus a smaller formation energy was found.
II. Possible Sources of Error and Provisions Taken for their Elimination

Reference has been made at various places in the thesis to possible sources of error and the provisions that were made to either eliminate them or calculate their magnitudes. Here a more detailed discussion will be presented, along with an elaboration of the experimental methods used.

The major source of error which could not be avoided experimentally is that which derives from the uncertainty of the quench temperature in quenching experiments. For annealing experiments, the complex nature of the quenched-in defects and the basic limitation of potentiometer sensitivity were the major sources of uncertainty. Some of these have been discussed on Pages 14 to 17 and Page 20, and will be dealt with in more detail below.

In addition to these, consideration has also been given to the following points: (1) retention of vacancies during quenching, (2) equality of specimen and dummy lengths, (3) constancy of liquid nitrogen bath temperature, and (4) thermal emf's.

1. Retention of vacancies during quenching

As the quench rate measurements have shown (Appendix I) there was a slower air quench preceding the true water quench. This initial air quench could not have been eliminated by changing the liquid quench medium. Quenching the specimen with a blast of liquid nitrogen into a vacuum vessel was considered; however, because of technical complications this was not pursued further.

In the calculation of $E_f$, a correction in this regard had already implicitly been provided. The only assumption made in connection with the escape of vacancies during the quenching and transferring periods was that the number of vacancies so escaped was proportional to the vacancies present,
i.e. Concentration of vacancies at temperature T: \[ \Delta n \approx n \cdot e^{-\frac{E_f}{kT}} \]

Vacancies escaped per unit volume: \[ r\Delta n = fn \cdot e^{-\frac{E_f}{kT}} \]

Vacancy concentration retained and measured: \[ (1-f)\Delta n = (1-f)n \cdot e^{-\frac{E_f}{kT}} \]

Thus, if \( \ln \Delta \rho \) is plotted against \( T \) and the slope is measured, the constant coefficient \((1-f)n\) does not appear and hence \(E_f\) is not affected.

(2) **Equality of specimen and dummy lengths**

The balanced condition for Bauerle and Koehler's circuit is:

\[ r_{si} - r_{di} + r_{st} - r_{si} = \int_{-\infty}^{\infty} \left( \frac{l_s}{A_s} - \frac{l_d}{A_d} \right) + \int_{-\infty}^{\infty} \left( \frac{l_s}{A_s} - \frac{l_d}{A_d} \right) = 0 \]

where \( \rho_i \) is the impurity resistivity, \( \rho_t \) is the thermal resistivity, \( l \) is the length and \( A \) is the cross-sectional area of the specimen. Thus if the length condition, \( \frac{l_s}{A_s} - \frac{l_d}{A_d} = 0 \), is not satisfied then errors result not only from the thermal part of the resistivity but also, and more seriously, from the impurity part itself. Physically there is no way to make \( l_s \) and \( l_d \) exactly equal. For any set of experiments, specimen and dummy wires were cut from the same wire. The diameter of the wire was measured twice every half centimeter along the length. To ensure the uniformity of heating between the potential leads, 20 cms lengths were needed both for the specimen and for the dummy. Silver wires of 0.002 inch in diameter were spot-welded onto each of them about 5 cms apart as potential leads. These specimens were stretched on a glass platform of travelling microscope and the lengths between the potential leads were measured. Five figures were taken, the last one was estimated from the fraction on the vernier scale and was not really significant. The fourth figure of the length of a specimen, in general, may differ with that of the corresponding dummy specimen by a small number; non-matching wires were discarded. The two matched wires were then mounted on the frame which was also made of pure silver, and the assembly was immersed in a liquid air bath.
The same current was sent through the specimen and the dummy in a series arrangement and \( r_s \) and \( r_d \) were measured. This measurement was, of course, repeated with reversed current. The \( r_d/r_s \) ratio was then compared with \( l_d/l_s \) ratio. The first three figures were always identical but the fourth figure often differed. If the potential leads were attached obliquely or the spot welding point was deformed to some extent the third figure was affected. In that case the specimen was again discarded.

Further correction for varying lengths for the balanced circuit was made by taking initial readings of \( V_{12} \), \( V_{34} \), and \( I \) on the virgin specimens before heating. The initial resistance difference \( \Delta r_{so} = \frac{(V_{12} - V_{34})}{I} \) thus obtained was regarded as the zero reading and was used to correct the subsequently quenched values of \( \Delta r_s \)'s. For the series circuit, the resistance of the quenched specimen was multiplied by the \( r_d/r_s \) ratio before subtraction of the dummy resistance.

(3) **Constancy of liquid nitrogen bath temperature**

In any one run the measurements were carried out in the following sequence:

\[
T \leftarrow I \rightarrow V_s \rightarrow I \rightarrow V_d \rightarrow I \rightarrow T
\]

Excluding the time required for the temperature and the current to attain their respective equilibrium values, a series of measurements required from three to five minutes. Measurements were repeated with reversed current. The liquid nitrogen was in contact with air for at least one hour before actual measurements were started. The boiling point of liquid nitrogen is \(-195.8^\circ C\) and that of liquid oxygen is \(-182.9^\circ C\). It is not known just to what extent and at what rate the oxygen gas in the air would condense or dissolve in the liquid nitrogen in five minutes. However, even if one were to
assume an exaggerated value of a 6 degree temperature increase (corresponding to the 50:50 mixture) during a 12 hour interval, then assuming a constant condensation or dissolution rate, the temperature change would be \( \frac{6}{12} \times 5 = 0.04 \)° C. during the 5 minutes required for the measurements. Now the change in electrical resistivity per 1° C. for pure silver between -100 to -200° C. is about 0.006 \( \mu \Omega \cdot \text{cm} \). Thus for a change in bath temperature of 0.04° C., the corresponding change in the electrical resistivity is about 2.4 \( \times 10^{-10} \) ohm·cm and this would register as about 0.1 μv on the potentiometer, which is within the uncertainty limits for the measurements.

(4) Thermal emf's

During the measurements the liquid air surface was kept about two inches above the end joints of the outside lead wires to the frame, which was cut from the same material, of same length and soldered onto the frame at places close together. In Bauerle and Koehler's balanced circuit, the currents and the potentials were arranged in a symmetrical and parallel manner electrically and geometrically and the two arms were kept at the same depth under the liquid air surface. Thus the thermal emf's developed in any part of the specimen cancelled out in the corresponding part of the dummy. In the series circuit, the technique of reversing the sample current and the potentiometer battery was followed.

Next, consider the adequacy of the methods used in the annealing experiments. The problems involved were: (1) the adequacy of the data of figure 8, (2) adequacy of the single slope change method for Em, (3) desirability of isochronal recovery experiments. The limited sensitivity of the available apparatus and the complex nature of the quenched in defects are pertinent to a discussion of these sources of error.

(1) It has been suggested that the recovery curve of figure 8 should have three or four times as many points to establish a dependable exponential relationship.
Even disregarding the uncertainty associated with the short annealing time described in the thesis Pages 18 to 20, attempts to provide a greater number of points on these curves were unwarranted because of the limited sensitivity of the potentiometer available. This can be seen as follows. Most specimens were .0127 thousandth of an inch in diameter (the specimen for figure 8 has a diameter of 14.3 thousandth of an inch) and a 5 cms length between the potential leads was used. Thus: 

\[ R = \frac{l}{\eta} = \frac{5 \rho}{\frac{.01272 \times 2.54}{2}} = 6100 \rho \]

For a measuring current of about 50 ma, to develop a potential difference of one microvolt would require an increase in the quenched in resistivity of

\[ 1 \mu \text{V} = 10^{-6} \times Ri = 6100 \rho \times 0.05 = 305 \rho \]

whence:

\[ j = \frac{10^{-6}}{305} = 3 \times 10^{-9} \text{ ohm-cm}. \] (For the specimen in figure 8 the corresponding quantity is 4.2 \times 10^{-9} \text{ ohm-cm}.) From figure 8 the resistivity difference between two neighbouring points was in the range of 10 \times 10^{-10} to 15 \times 10^{-10} \text{ ohm-cm} which in terms of potential difference would only amount to 0.33 to 0.5 \mu \text{V}. If this quantity was to be further divided into three or four parts, then the difference would be only 0.1 to 0.16 \mu \text{V}. A quantity of this magnitude could not be measured with sufficient accuracy using the present apparatus.

(2) Other values of Em determined by change in slope methods are listed in table. These values were determined from separate quenches; one determination for each quench. The reason for employing this technique was that in the initial stage, the annealing rate was always too fast to be determined and thus the change in slope method was not applicable while in the later stage, the annealing rate was so sluggish that the decreases in resistivity within reasonable time intervals were negligible.
The use of higher annealing temperatures was precluded because of the possible effects on dislocations. Thus a restricted region only could be utilized.

The large variations of the $E_m$ values originate (1) from the statistical error due to the limited accuracy of the measurements and (2) from the fact that, since these values were determined from different quenches the defect composition could not be expected to be the same and thus each value should be regarded as unique. For the latter reason it was thought not proper to calculate standard deviations from them and hence no statistical errors were given in the thesis.

(3) The desirability of isochronal annealing experiments to determine the details of recovery stages, merits some discussion. Conclusions that can be drawn from isochronal annealings normally can also be inferred from isothermal annealings. In fact, if the quench temperature were precisely controlled during a series of isothermal annealings at various temperatures, the isothermal annealing curves could be transformed into isochronal annealing curves. Some isothermal annealing data were obtained; however, this was not presented in the thesis because it did not provide any additional information. The general features were all alike: the initial rate was always very fast even at temperatures as low as 0-5°C, while a few minutes later it became very slow.
This was also true for temperatures as high as 60° C. A time interval suitable for the initial stage was not suitable for the later stage; therefore the annealings were not carried out at equal intervals. Also, since the quench temperature could not be accurately controlled, the quenched in resistivity was not exactly reproduceable and moreover, the composition of defects, (vacancies, vacancy-clusters and/or dislocations) may also have differed for one quench from another. The latter condition, precludes the use of the isochronal method.

Finally, it has been pointed out that it is improbable that a vacancy could combine with another vacancy or be removed at a sink before interacting with a gold atom since the concentration of vacancies was of the order of 0.01% and of sink sites $10^{-5}$% while the gold concentration was 2%. However, the significant factor here is not simply the relative probabilities for a vacancy to encounter another or for it to encounter a gold atom but rather the resultant probability that a number of vacancies will interact with the gold atom which may then diffuse to ordered positions with other gold atoms. Only then does the effect of vacancy - gold atom interaction register in resistivity measurements. It can be easily shown that, in the face centered cubic alloy of the above composition a vacancy will, on the average, encounter a gold atom on every third step whereas 30 to 40 steps are required before it can encounter and combine with another vacancy. Now for the first jump of the gold atom we may assume that a vacancy is readily available. However, for a meaningful second jump the gold atom must encounter another vacancy which moves in from the forward direction. For the gold atom to move three times in the forward direction, the probability is proportional to the cube of the vacancy concentration, i.e. $(10^{-4})^3$. Since the gold concentration is $2 \times 10^{-2}$, the resultant probability is $2 \times 10^{-14}$. 
On the other hand, for a vacancy to meet another, one must move 30 to 40 times. However, once they do meet, they combine and the effect on resistivity measurements is immediate. The resultant probability of such a process is therefore $(10^{-4})^2$ which is considerably larger than that above. Thus, calculations demonstrate qualitatively that divacancy formation is not improbable.