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Quenched Resistance in Dilute Gold-Tin and Gold-Silver Alloys*

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In order to investigate the effect of impurities on the resistance quenched into gold wires, dilute alloys of gold-silver and gold-tin were quenched and the resulting data compared with that for pure gold. Data on the resistance quenched into 0.002-in.-diam pure gold wires quenched in helium and air are presented and compared to previously published data on the resistance quenched into 0.016-in.-diam gold wires quenched in water and glycol. The resistance quenched into gold-0.01 and 0.1 at. %-silver alloys is the same, within experimental error, as that quenched into pure gold. The resistance quenched into gold-1.0 at. %-silver alloys agrees with the pure-gold data for high-quench temperatures, but appears to fall below the pure-gold data at low temperatures. It is suggested that the result is consistent with a vacancy-silver binding energy in gold of less than 0.15 eV. The resistance quenched into gold-0.03, 0.1 and 0.3 at. %-tin alloys is greater than that quenched into pure gold for quench temperatures below 700°C. In the vicinity of 700°C the resistance quenched into the two lowest tin-concentration alloys is indistinguishable from the pure-gold data, and the resistance quenched into the gold-0.3 at. %-tin alloy actually appears to fall below the pure-gold data. Unfortunately, the results obtained are inconsistent with the usual model proposed for such alloys; the data cannot be described solely in terms of a vacancy-impurity binding energy, and no value for such a binding energy can be deduced. Some cautionary points concerning the interpretation of previously published binding energies between vacancies and impurities are noted.

I. INTRODUCTION

IN recent years, a wide variety of techniques have been employed to investigate phenomena associated with the production and motion of point defects in metals. Gold has frequently been studied because it may be obtained in high purity, is easy to fabricate, has a low solubility for gases, does not form an oxide, and, as a one-electron solid, is amenable to treatment using the most reliable theoretical models for metals. The point defect most important in describing the high-temperature properties of gold has been determined to be the lattice vacancy. Although the enthalpies of formation and of motion for a vacancy in gold now appear to be fairly well established,[1] the interaction energies between a vacancy and an impurity present in dilute solution in gold have not yet been satisfactorily established for any impurity.

Diffusion studies[2] suggest that the interaction between a vacancy and an impurity in gold is much smaller than the formation energy of a vacancy of 0.98±0.02 eV. In fact, the theory of Lazarus,[3] a modified version of which has been shown by LeClaire[4] to give a satisfactory fit to a wide range of diffusion data taken on noble metal alloys, predicts binding energies between impurities and a vacancy in gold which are typically less than 0.05 eV; for tin in gold Lazarus predicts a binding energy of 0.06 eV, and for silver in gold, LeClaire[5] predicts a binding energy of 0.02 eV. However, the results of a more recent calculation by Flynn[6] suggest the possibility that the Lazarus model may underestimate the binding between a vacancy and an impurity. Using a different model, Flynn derives a binding energy between a vacancy and a tin impurity in silver of 0.17 eV. A similar value would be expected for tin in gold.

Although three sets of measurements have been reported on quenched alloys of silver in gold, the binding energy between a silver atom and a vacancy in gold is not yet clearly established. Cattaneo and Germagnoli[7] suggest a binding energy of about 0.3 eV from an analysis of some rather complex annealing behavior of the quenched alloys. Kloske and Kauffman,[8] on the other hand, propose a binding energy of less than 0.05 eV from a study of quenched-in resistance as a function of quench temperature and a study of the subsequent room-temperature annealing behavior of the quenched-in resistance. Unfortunately, Kloske and Kauffman made no pure-gold measurements to compare with their alloy results, and the energies that they used for pure gold do not appear to be the appropriate ones for their analysis. Asimow[9] used alloys of such high silver content that he obtained effects which he interpreted as being due to short-range ordering of the silver atoms, and which obviate any use of his data for determining a binding energy.

One quenching study has been made on alloys of palladium in gold using concentrations of palladium of 1 at.% and greater.[10] The data obtained do not appear

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[1] C. P. Flynn, J. Bass, and D. Lazarus, Phil. Mag. (to be published).

[2] D. Lazarus, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 71.

[3] D. Lazarus, Phys. Rev. **93**, 973 (1954).

[4] A. D. LeClaire, Phil. Mag. **7**, 141 (1962).

[5] A. D. LeClaire, paper presented at Conference on Electron Structure of Metallic Solid Solution, Sheffield, 1963 (unpublished).

[6] C. P. Flynn, Phys. Rev. **125**, 881 (1962).

[7] F. Cattaneo and E. Germagnoli, Phys. Rev. **124**, 414 (1961).

[8] R. Kloske and J. W. Kauffman, Phys. Rev. **126**, 123 (1962).

[9] R. M. Asimow, Phil. Mag. **9**, 171 (1964).

[10] Y. Hamaguchi, J. Phys. Soc. Japan **16**, 1692 (1961).

to have a simple interpretation in terms of only a binding energy; Asimow has suggested a possible qualitative interpretation in terms of short-range ordering of the impurities.

In addition to these studies of gold alloys, a substantial amount of work has been concerned with the interaction between vacancies and impurities in aluminum alloys.[11] Unfortunately, little diffusion work has been done on aluminum and aluminum alloys, and the theories mentioned above are not applicable to aluminum. Thus, there presently exist no independent checks for the quench data taken on aluminum alloys.

The present paper presents studies of the resistance quenched into gold–0.01, 0.1, 1.0 at.%-silver alloys, and gold–0.03, 0.1, 0.3 at.%-tin alloys. Silver was chosen as one solute because it is similar to gold and should serve as a minimal perturbation. The gold-silver alloy is also not strongly affected by being heated in air. Tin was chosen as the other solute to serve as a large perturbation, and because it is soluble in gold to several at.% and has a vapor pressure sufficiently small that it would not evaporate appreciably during specimen preparation and handling.

In order to determine the specific effects caused by the impurity, the resistance quenched into the alloys is compared to that quenched into pure gold which has been treated in identically the same manner as the alloys. A detailed analysis of the resistance quenched into 0.016-in.-diam pure gold wires was presented in a previous paper.[1] The resistance quenched into 0.002-in.-diam pure gold wires is given in the present paper and compared to the 0.016-in.-diam gold data.

II. EXPERIMENTAL PROCEDURE

A. Quenching Apparatus

Two different quenching techniques were used; one for 0.016-in.-diam gold and gold-silver wires, and the other for 0.002-in.-diam gold and gold-tin wires.

The procedure used for the larger wires was similar to that described by Bauerle.[12] A 17 cm length of wire, suitably bent to minimize quenching strain, was attached to a copper holder and suspended 2 to 3 cm above the quenching fluid, inside a covered container. The gauge length was determined by two 0.002-in.-diam pure gold wires spot-welded 3 to 4 cm apart near the middle of the wire. Following an annealing procedure, the wire was resistance heated and quenched by switching open a relay, allowing external wires to spring the holder and specimen into the bath. The microswitch that activated the relay could also be used to trigger an oscilloscope, which then displayed the voltage across the gauge length during the quench. This display of voltage at constant current gave the resistance of the specimen as a function of time. From the known dependence of the resistance of gold on temperature, changes of the average temperature across the wire during the quench could be determined.

As the tin content of the gold-tin alloys would be depleted by heating in air, it was necessary to use a different technique to obtain satisfactory results. The basic procedure used was similar to that developed by Doyama[13] for quenching studies of pure silver. A 10-cm long wire of 0.002 in. diam was suspended inside a Pyrex bulb of inner diameter either 55 or 60 mm. The gauge length was determined by two 0.0006-in.-diam wires, of the same material and nominal purity as the specimens, spot-welded about 5.9 cm apart. A Plexiglas holder with two holes 5.9 cm apart was used to give a gauge length reproducible within ±0.1 cm in order to minimize effects of different gauge lengths in comparing results obtained from different specimens. The Pyrex bulb was sealed to a Pyrex vacuum system and evacuated to a pressure of about 10^{-8} mm Hg. A tantalum getter inside the bulb was then heated for a few minutes to 1700°C, a temperature allowing some outgassing of the getter without causing significant contamination of the specimen. The specimen bulb was then sealed off from the vacuum system and filled with pure helium. Finally, the specimen bulb was immersed in liquid introgen to increase the amount of helium in it, and then sealed off. The tantalum getter was heated to 1200°C for about an hour, with the specimen bulb at room temperature, in order to remove as much of the residual gases, other than helium, as possible. The adequacy of the gettering procedure was checked by comparing the change in resistance at liquid-helium temperature of specimens given the usual three-day annealing procedure described below when present in gettered and ungettered bulbs. Specimens in bulbs which had been gettered lost less than 1% of their resistance at liquid-helium temperature during such an anneal. A specimen in an ungettered bulb lost over 25% of its resistance after a similar treatment.

In this second system, the specimen wire was quenched by switching off about 95% of the heating current, while the helium-filled bulb was immersed horizontally in a liquid nitrogen bath. The voltage at constant current across the gauge length was displayed as a function of time during the quench on an oscilloscope triggered by the onset of the quench.

B. Materials and Specimen Fabrication

All gold used was nominally 99.999% pure (Sigmund Cohn Company), with a resistivity at 25°C of 2.25 ±0.05 μΩcm, consistent with the best values reported for gold.[14] The 0.016-in.-diam gold wires had a ratio of over 2000 after being annealed in air. The 0.002-in.-diam

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[11] For a summary of published binding energies, see D. R. Beamon, R. W. Balluffi, and R. O. Simmons, Phys. Rev. **134**, A532 (1964).

[12] J. E. Bauerle and J. S. Koehler, Phys. Rev. **107**, 1493 (1957).

[13] M. Doyama and J. S. Koehler, Phys. Rev. **127**, 21 (1962).

[14] A. N. Gerritson, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956).

wire had a resistance ratio of about 700 after being annealed in air, but only about 500 after being put into the specimen bulb and taken through the usual procedure preparatory to quenching. Spectroscopic analysis (kindly performed by John Walters of the Department of Chemistry, University of Illinois) showed the major impurities in the as-supplied wire to be copper and silver in amounts consistent with the quoted purity. Spectroscopic analysis of some 0.002-in.-diam specimens which had been through the usual prequench procedure showed an additional few parts per million of silicon and magnesium, which probably came out of the Pyrex during bakeout. Although one might have expected to contaminate the specimens with tantalum and tungsten, the other materials present in the bulb, no traces of either material were observed.

Gold-silver alloys with silver concentrations of about 0.01 and 0.1 at.% were obtained from the Battelle Memorial Institute. A gold-1.0 at.%-silver alloy was obtained from the Western Gold and Platinum Company. A spectroscopic analysis provided with this last alloy showed that the major contaminants present were Al, Ca, Pd, Fe, and Si in a total concentration of a few parts in 10^5.

One alloy of gold-0.1 at.%-tin was obtained from the Sigmund Cohn Company. Although the resistance at liquid-helium temperature of this alloy was about two and one-half times as large as expected for the tin concentration claimed, spectroscopic analysis (Lucius Pitkin, Inc., Accurate Metal Laboratories, and Detroit Testing Laboratory, Inc.) showed no significant concentration of other impurities. In addition, three independent spectroscopic and chemical analyses, while not in good agreement, suggested that the tin concentration was 0.1±0.05 at.%.

Four alloys of gold-tin, containing 0.03, 0.1, 0.3, and 1.0 at.% tin were made in this laboratory from 99.999% pure gold and 99.99% pure tin. The correct amount of each metal was weighed out and put into a spectroscopically pure graphite crucible which had previously been given an *aqua regia* bath, a water bath, and a high-temperature bakeout to remove possible impurities. The crucible was capped and sealed off under vacuum of better than 10^{-4} mm Hg in a Vycor tube. The tube was placed in a furnace that could be rocked back and forth to facilitate mixing of the constituents. After a specimen was melted and well mixed, it was quenched into water to insure rapid cooling. The alloy cylinders so produced were sent to the Western Gold and Platinum Company for drawing into 0.002-in.- and 0.0006-in.-diam wire for use as specimens and potential leads, respectively. Spectroscopic analysis of the finished specimens showed that no additional impurities in greater concentration than a few parts per million had been introduced by the fabrication procedure. The resistivity of the tin in these specimens is plotted in Fig. 1 as a function of tin concentration along with some values determined by Linde. The resistivity of the tin in the gold—0.1%-tin wire supplied by Sigmund Cohn is shown on the same plot. The disagreement is not understood. Spectroscopic analysis of our specimens (Accurate Metal Laboratories and Detroit Testing Laboratory, Inc.) confirmed the concentrations of the 0.03 and 0.3% alloys. Disagreement between the two different analyses led to the assignment of a concentration of 0.10±0.03 at.%-tin to the nominally 0.1% alloy. The concentration of tin in the 1.0% alloy was confirmed by chemical analysis.

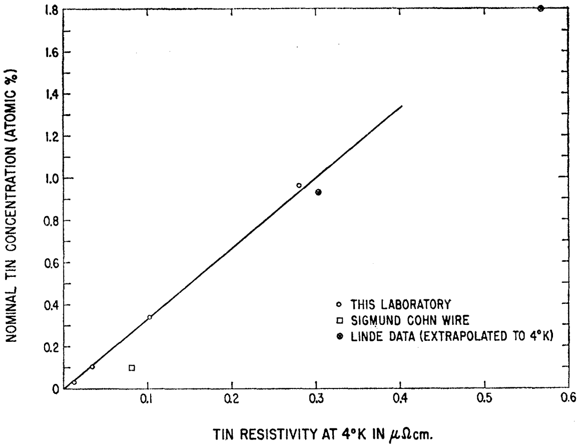

FIG. 1. Resistivity of tin at 4°K, when present as an impurity in gold, as a function of tin concentration.

All specimens were resistance heated and their temperatures determined from the ratio of the resistance at the quench temperature to that at 17.3°C. These resistances were determined from measurements, on a Rubicon No. 2780 potentiometer, of the voltage across the specimen gauge length and across a standard resistor through which the measuring current was passed.

For pure gold, the data of Meechan and Eggleston[15] and Northrup[16] were used as standards. Unfortunately, the data of Dominicali and Christensen,[17] Misek and Polak,[18] and Holborn,[19] while not mutually consistent, do not agree with those used here. However, since the temperature of the alloys was determined in terms of the same temperature scale used for the pure gold, and the resistance quenched into the alloys is compared to that quenched into pure gold, minor systematic errors in the pure-gold temperature scale should not cause important errors in the resulting data.

In order to conform with the data of Krautz and Schultz,[20] the measured resistances of the gold-silver alloys were corrected to equivalent pure-gold resistances

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[15] C. J. Meechan and R. R. Eggleston, Acta. Met. **2**, 680 (1954).

[16] E. F. Northrup, J. Franklin Inst. **177**, 1 and 287 (1914).

[17] C. A. Domenicali and E. L. Christenson, J. Appl. Phys. **32**, 2450 (1961).

[18] E. Misek and J. Polak, J. Phys. Soc. Japan **18**, Suppl. II 179 (1963).

[19] L. Holborn, Ann. Physik **59**, 145 (1919).

[20] V. E. Krautz and H. Schultz, Z. Naturforsch. **9a**, 125 (1954).

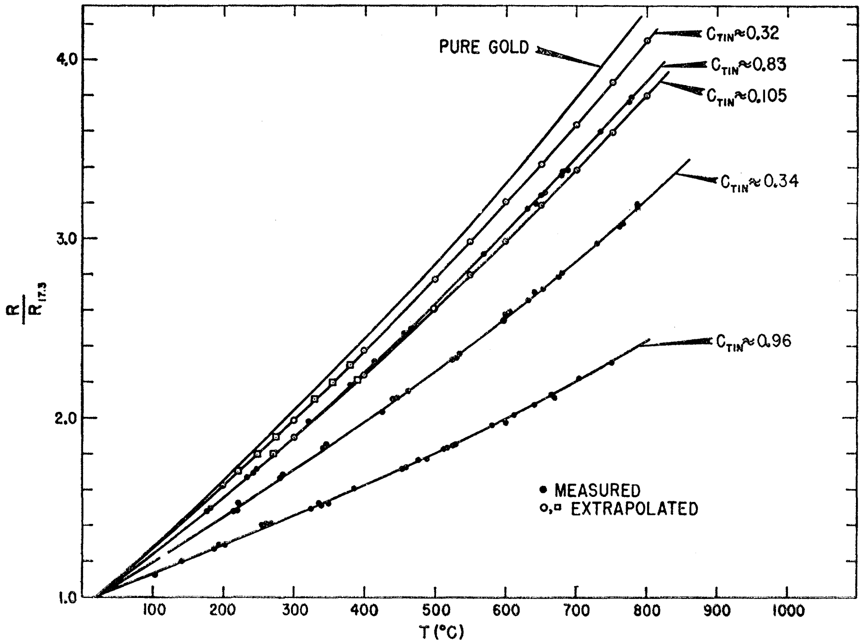

Fig. 2. Ratio of the resistance of gold-tin alloys at temperature T to that at 17.3°C plotted as a function of temperature.

by subtracting 1.07 times the resistance of the alloy at liquid-helium temperature from the resistance at all other temperatures. These corrected resistances were then compared, as described above, with the resistance-ratio data for pure gold. This procedure gives a temperature scale that differs from one determined for the highest silver concentration alloy using Matthiessen's rule by only about 6°C at the highest temperatures. The difference is less at lower temperatures, and is negligible at all temperatures for the two alloys with lower silver content.

Since no comparable data were available for gold-tin, it was necessary to measure the temperature dependence of the resistance of some such alloys. The resistances of gold-0.083, 0.34, and 0.96 at.%-tin alloys were measured as a function of temperature using pure gold to determine the temperature scale. These alloy concentrations were determined in a self-consistent manner from the data taken in this laboratory.

Two 2-in. long, 0.002-in.-diam wires, one of pure gold and one of gold-tin, were suspended side by side in a vertical vacuum furnace evacuated to a pressure of less than 2×10^{-5} mm Hg. After an anneal to remove the effects of drawing, the wires were heated in stages to a temperature of 750 to 800°C, and the resistance of each wire measured at each stage. A similar procedure was followed during cooling.

Because of tin loss at the highest temperatures, some corrections had to be made to the highest temperature data. These corrections never exceeded 10°C. No evidence of specimen length change during the measuring procedure was found, and the gold wires maintained sufficient purity to allow useful data to be obtained. It is estimated that the data are accurate to about 10°C for temperatures less than 600°C and to about 15°C at higher temperatures. A detailed discussion of the experimental procedure and error analysis is given in the thesis.[21]

Figure 2 shows the ratios of the alloy resistance at temperature T to that at 17.3°C calculated from the data. It is useful to note that Matthiessen's rule, when used in conjunction with resistance-ratio data for pure gold, appears to determine the temperature of dilute alloys of tin in gold to an accuracy of 10 to 15°C for temperatures up to 800°C. This is true in spite of the fact that the resistance of the tin impurity is not independent of temperature; it increases by about 15% from liquid-helium temperature to 300°C in gold-1.0%-tin alloys.

All new specimens were given an initial high-temperature anneal to promote grain growth, minimize dislocation content, and generally remove the effects of drawing.

The 0.016-in.-diam pure gold wires were given anneals varying from 30 min at 850°C to 2 h at 1000°C with no appreciable difference in effect on either the grain size, the resistance ratio ($R_{25°C}/R_{4°K}$), or the subsequent behavior of the wire. In all such wires the resistance ratio was about 2200 and the grain size varied from 0.002 to 0.010 in. across, with an average smallest dimension of 0.005±0.001 in.

The 0.016-in.-diam gold-silver alloys were given anneals of about half an hour at 900°C. This procedure gave an average grain size of about 0.004±0.001 in.

The 0.002-in.-diam pure gold and gold-tin wires were generally annealed for about half an hour at 650 to

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[21] J. Bass, thesis, University of Illinois, 1964 (unpublished).

700°C and then overnight at 500°C. The average grain size appeared to be about 0.001 in., although it was often difficult to see the grain structure of the specimens.

In addition to this initial anneal, each specimen was given a cleansing anneal prior to each quench series to remove residual vacancies, vacancy clusters, and dislocations left from previous handling. This procedure was necessary to equilibrate the vacancy concentration of the specimen at a temperature low enough to serve as a vacancy-free base.

The 0.016-in.-diam pure gold and gold-silver alloys were given cleansing anneals of five min at above 800°C, five min at 500°C, and 15 min at 300°C. This procedure allowed satisfactory reproducibility of the "vacancy-free" resistance at liquid-helium temperature which was subtracted from all quenched-in resistances to give the quenched-in resistance increment.

The 0.002-in.-diam pure gold wires were given one of two cleansing anneal procedures. One, of 15 min at 650 to 700°C, 5 min at 500°C, and 15 min at 300°C, allowed a base to be obtained which was sufficiently reproducible to allow analysis of quenches from above 450°C. The other, a substantially longer version of the same procedure, was used to simulate the annealing procedure necessary for cleansing the gold-tin alloys. This procedure allowed data to be obtained for temperatures below 450°C, but at the expense of a strictly reproducible base. At temperatures above 450°C, the two procedures give the same quenched-in resistance within experimental error.

The annealing procedure necessary to produce a "vacancy-free" state in the gold-tin alloys was rather more prolonged. Typically the specimen was annealed at about 700°C for 15 min to half an hour, then at about 600°C overnight. The next day it was turned down to 500°C for a few hours, to 400°C for a few hours, and then left overnight at 300°C. It was annealed at 250°C and 200°C for half a day each. Finally, it was left overnight at 150°C and sometimes all day at 100°C before being turned down to room temperature. While this procedure did not result in a precisely reproducible base—the resistance at liquid-helium temperature usually decreasing by $\frac{1}{2}$ to 1% of its initial value after such an anneal—it did lead to reproducibility of the quenched-in resistance increments measured from the base determined after the annealing procedure. These quenched-in resistance increments were measured at a series of increasing temperatures, with an occasional measurement repeated at the same quench temperature or at a lower temperature to check the reproducibility of the quenched-in resistance.

When the annealing procedure for hard-drawn wires was finished, the wires were heated until they glowed and examined for temperature inhomogeneities. Those wires which showed no significant temperature distribution along the gauge length were prepared for quenching. In addition to this initial inspection, the 0.002-in.-diam wires were similarly examined before each quench series, and the 0.016-in.-diam wires were inspected while glowing before each individual quench. Only wires with no visible temperature inhomogeneities along the gauge length were quenched.

After a quench, the specimen, in a holder or bulb was slowly and carefully precooled in liquid nitrogen and then immersed in a dewar of liquid helium. All measurements of quenched-in resistance were made at liquid-helium temperature. The quenched-in resistance associated with a quench temperature T was determined as the difference between the resistance of a wire quenched from T, and the resistance of the same wire after a cleansing anneal.

The resistances of the pure gold and gold-silver specimens were measured on a Rubicon No. 2767 Thermofree potentiometer, and those of the gold-tin alloys were measured on a Honeywell No. 2768 6-dial potentiometer. The measuring current, supplied by a bank of Willard No. DH-5-1 batteries, was maintained constant at 1 A for the 0.016-in.-diam specimens and at 0.05 A for the 0.002-in.-diam specimens. These currents caused no measurable heating of the 0.016-in.-diam wires or the 0.002-in.-diam pure gold wires, and a temperature rise of less than 0.2 C° in the 0.002-in.-diam gold-tin wires. Reversing procedures were used throughout the measuring process to eliminate the effects of the more constant thermal emf's.

In addition to measurements of the quenched-in resistance, some studies of the annealing out of this resistance were made to obtain additional information concerning the defects present. As no satisfactory data could be obtained from isothermal-annealing studies of the gold-tin alloys, only isochronal studies are reported here.

An isochronal anneal consisted of heating the specimen for a fixed time (e.g., 5 min) at a series of increasing temperatures, usually about 30°C apart, until most of the quenched-in resistance annealed out. The specimens were heated resistively, and the temperature controlled by controlling the current. It was possible to keep the temperature constant to within a few centigrade degrees with the equipment used, which was sufficiently constant for the purposes of the present experiment.

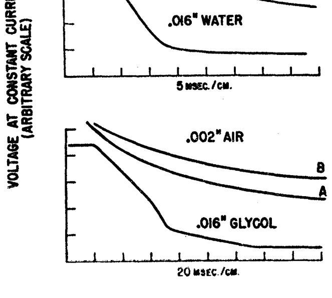

FIG. 3. Resistance versus time curves, drawn to scale, for quenches of 0.016-in.-diam and 0.002-in.-diam wires.

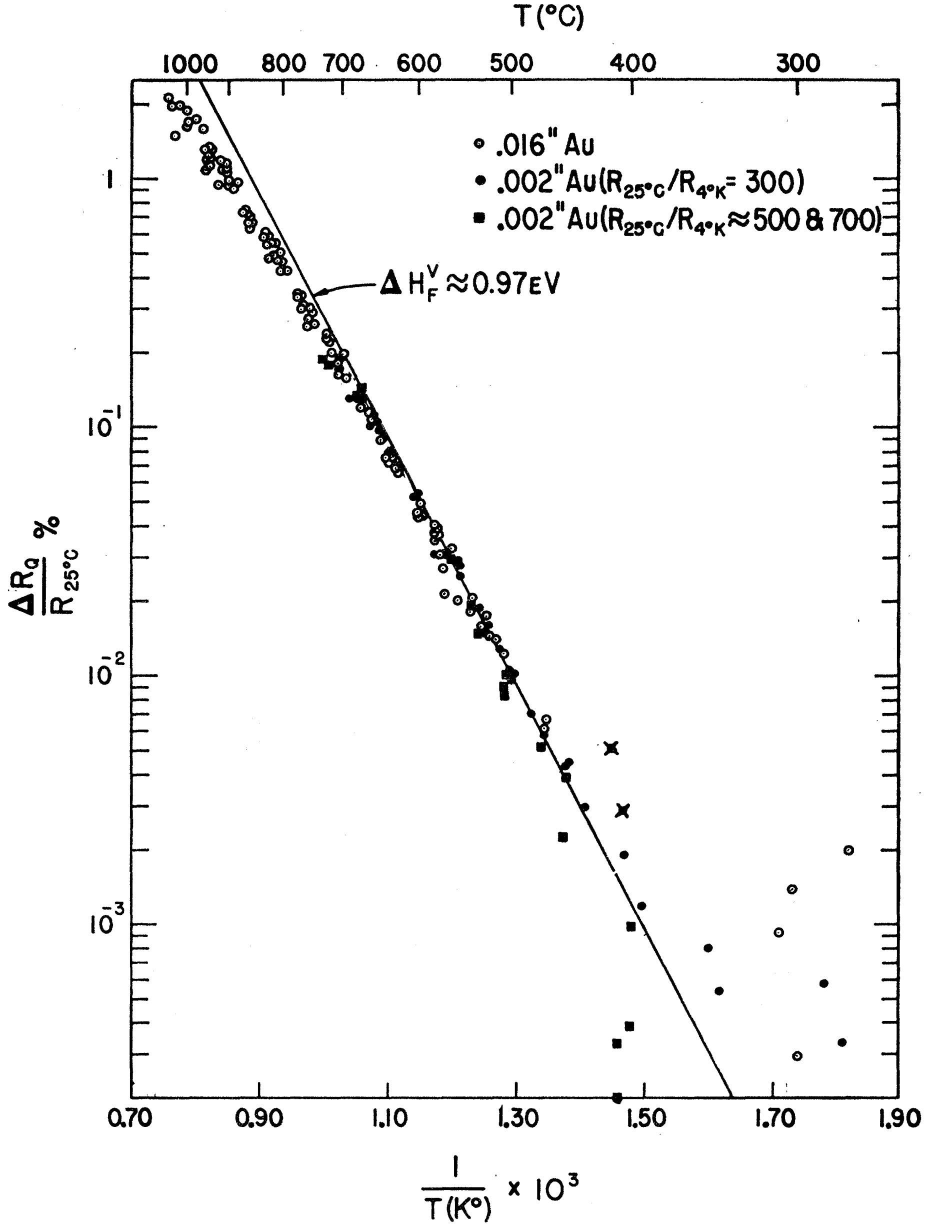

FIG. 4. Comparison of resistance quenched into 0.016-in.-diam wires quenched into water and 0.002-in-diam wires quenched in helium.

III. EXPERIMENTAL RESULTS

Figure 3 shows typical resistance versus time curves, drawn to scale, for quenches of 0.016-in.-diam wires from 700°C into water and glycol, and for quenches of 0.002-in.-diam wires from about 650°C in helium and air. As can be seen, the 0.002-in.-diam wires quenched in helium had about the same initial quench speed as the 0.016-in.-diam wires quenched into water, and the 0.002-in.-diam wires quenched to room temperature in air compared similarly to the 0.016-in.-diam-wire glycol quenches. The 0.002-in.-diam wires quenched in air-to-liquid-nitrogen temperature had a quench time about half that of the 0.016-in.-diam glycol quenches. Presumably this was due to the lower pressure of gas in the bulb at liquid-nitrogen temperature. The alloy quench times were indistinguishable from those for pure gold.

The resistance quenched into 0.016-in.-diam wires quenched into water and 0.002-in.-diam wires quenched in helium gas are compared in Fig. 4. In the temperature range where the two sets of data overlap, there appears to be no significant difference between them.

Data taken on 0.016-in.-diam wires quenched into glycol and 0.002-in.-diam wires quenched in air are compared in Fig. 5. Those 0.002-in. data designated by A, which had nearly the same quench time as the 0.016-in.

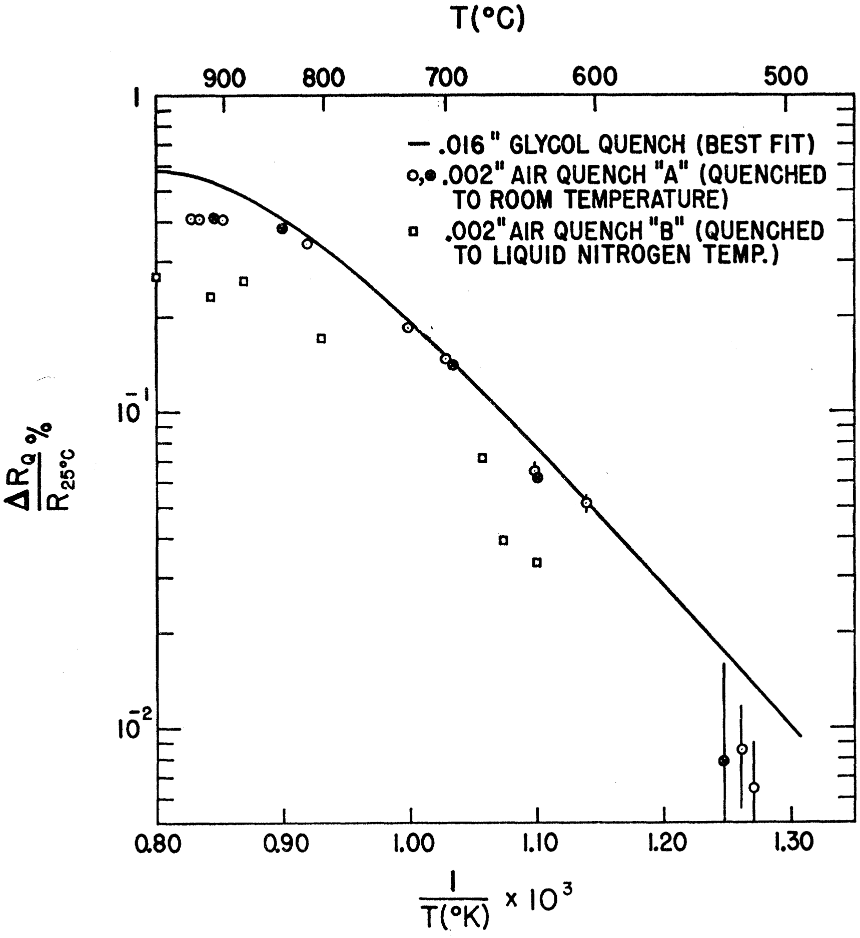

FIG. 5. Comparison of resistance quenched into 0.016-in.-diam wires quenched into glycol and 0.002-in.-diam wires quenched in air.

glycol-quench data, are in good agreement with the glycol data, although slightly less resistance seems to be quenched into the smaller wires. The 0.002-in.-diam data, designated by B, in which the quench time was about two times slower than for the glycol quenches, shows a significantly smaller quenched-in resistance.

Figure 6 shows the data of Bauerle and Koehler[12] and of Emrick[22] compared with the best fit curve for the present data. Bauerle's data have been corrected in an approximate manner for a systematic bias in the base determination, as discussed in the thesis.[21] Emrick's data presumably show the same effect, but could not be similarly corrected, and are thus presented with no base correction. However, a correction for a systematic temperature bias was made The base correction to Emrick's data would only be significant at low temperatures and would bring his data into closer agreement with the present results. In the present experiment, the quenched-in resistances were measured at liquid-helium temperature; Bauerle made his measurements at liquid-nitrogen temperature, while Emrick's were made at 0°C. Because of the close agreement between the data taken at three different temperatures, it is possible to set an upper limit for the temperature dependence of the vacancy resistance in the temperature range 4 to 273°K. The value $(1/R_v)(dR_v/dT) \leqslant 7\times10^{-4}(1/\text{C}°)$ is consistent with the data.

The results of water-quenching experiments on two concentrations of gold-silver alloys, containing about 0.01 and 0.1 at.% silver, respectively, are shown in Fig. 7. The heavy solid line is the best-fit curve for the 0.016-in.-diam pure-gold water-quench data, while the two light lines represent the maximum scatter obtained with the pure gold wires. The gold-silver data show no significant deviations from the pure-gold curve for either of these two silver concentrations.

Figure 8 shows the data obtained from quenching two gold–1.0 at.%-silver alloys into water compared to the pure-gold data. While these data agree with that for pure gold at high temperatures, the data taken on the first of the specimens falls below the pure-gold data at lower temperatures. More difficulty was encountered in obtaining a satisfactory "cleansed" base with the second wire, as evidenced by the larger error associated with the low-temperature point shown. Within the

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[22] R. M. Emrick, Phys. Rev. 122, 1720 (1961).

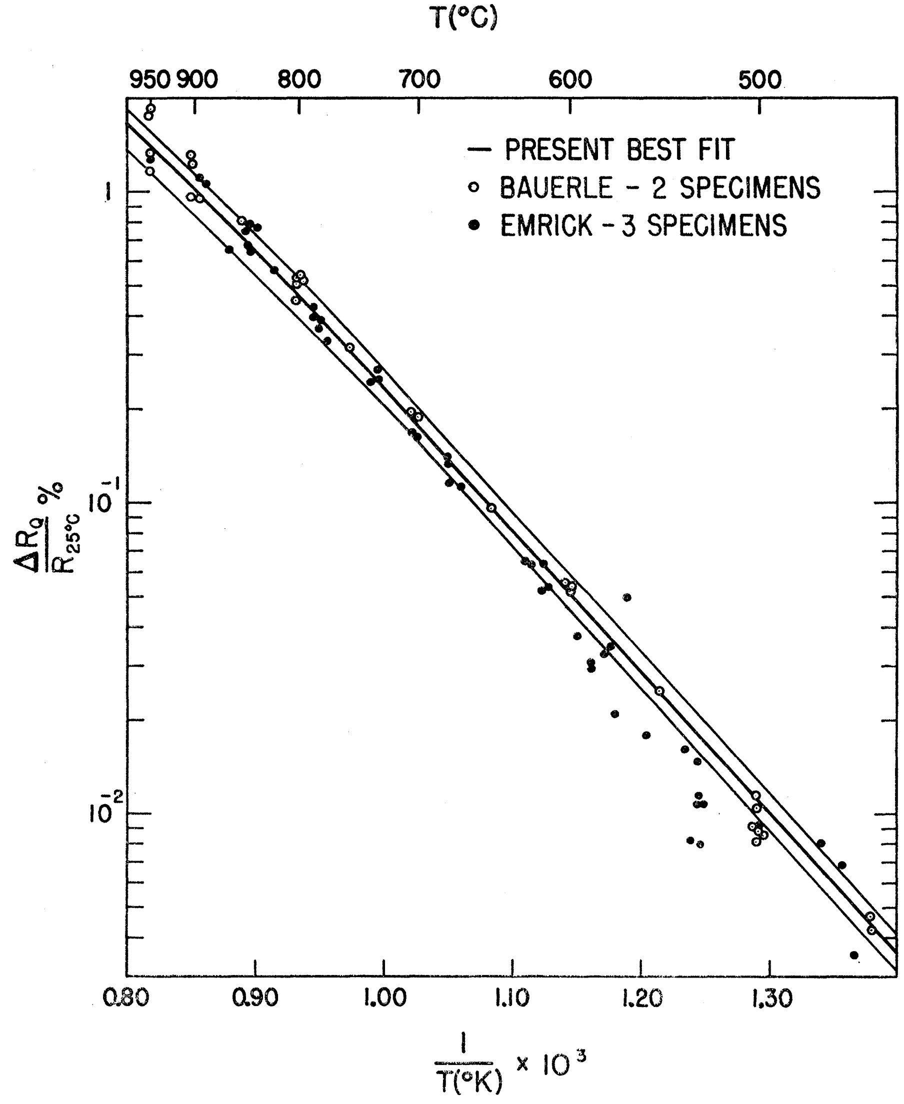

FIG. 6. The data of Bauerle and Koehler and of Emrick compared to the present data.

scatter of the data, this second wire shows no deviation from the pure-gold data.

Figures 9 and 10 show the resistance quenched into gold—0.03 and 0.3 at.%-tin alloys, respectively, compared to that quenched into pure gold under the same experimental conditions. The gold-data shown are those taken on wires which had been through the usual bake-out and gettering procedure used for the gold-tin alloys. This does not include the data taken on 0.002-in.-diam gold wires with a resistance ratio ($R_{25°C}/R_{4°K}$) of 700, which were not baked out or gettered. The low-temperature gold data shown were taken on two specimens with a resistance ratio of 300, which had been given a high temperature gettering—the getter was cleansed at 2100°C rather than the usual 1700°C. The quenched-in resistance obtained can probably therefore be considered as an upper limit on the pure-gold data. These low-temperature gold data are compared with those taken on a wire with a resistance ratio of 700 in Fig. 4.

In order to minimize confusion, the gold-tin data have been averaged, for each tin concentration, in groups of about 7 points each and plotted in Fig. 11. The vertical lines represent the average deviation of the points from the best-fit line, and the solid lines represent hand-drawn best-fit curves to the data. The complete data are given in the thesis.[21]

The temperature scale for the gold-0.1 at.%-tin alloy made by Sigmund Cohn was determined using Mathiessen's rule. This was noted above to be a reasonable approximation. Actually, the data taken on these alloys are only given to show that they are not in disagreement with the other data presented. The excellent agreement between the results for the Sigmund Cohn 0.1%-tin alloy and the 0.1%-tin alloy made in this laboratory depends on the temperature scale used for the Sigmund Cohn wire and is probably fortuitous.

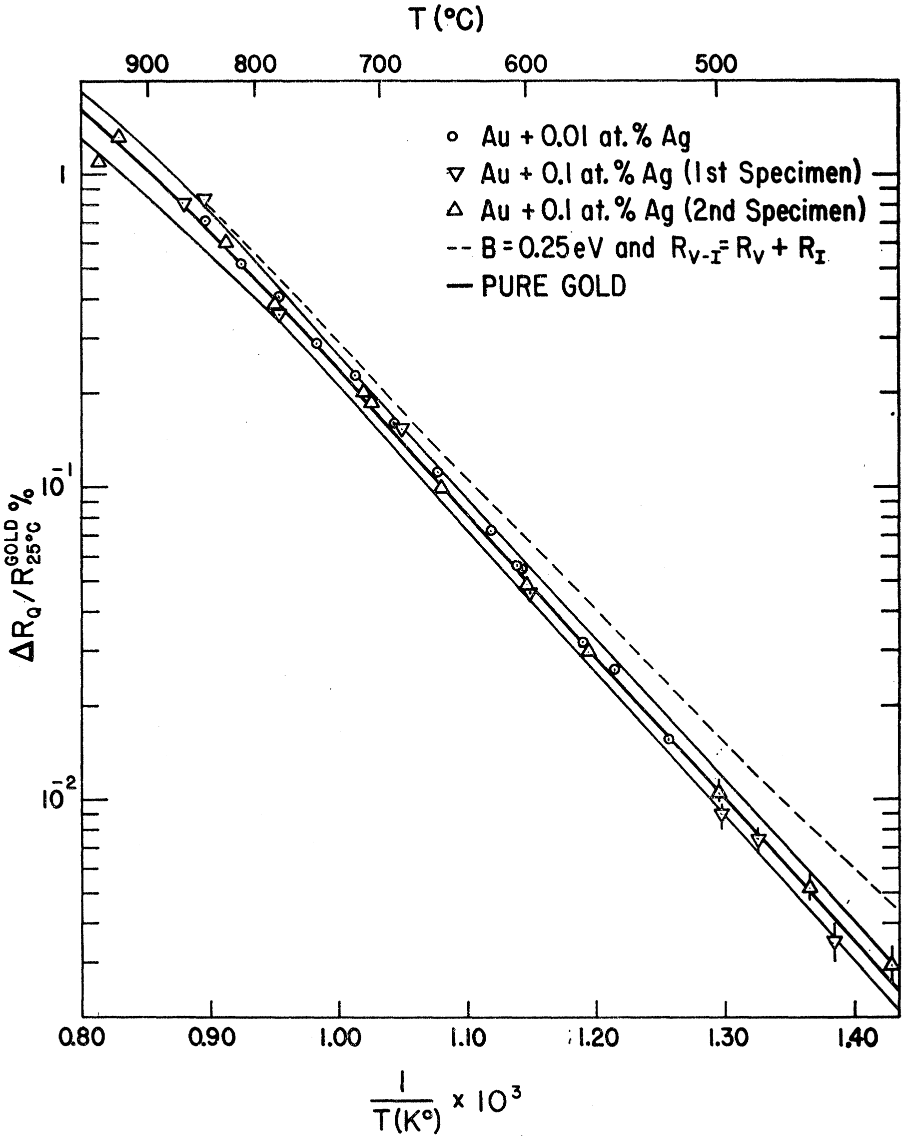

FIG. 7. The resistance quenched into gold-0.01 and 0.1 at.%-silver alloys compared to that quenched into pure gold.

Figure 12 shows isochronal annealing data taken on two sizes of gold wire quenched from about 650°C. The curves shown for 0.016-in.-diam wire with a resistance ratio ($R_{25°C}/R_{4°K}$) of 2200, are essentially the same whether the wire was quenched into water or glycol. While the curve for the 0.002-in.-diam wire with a resistance ratio of 700 is similar to that for the 0.016-in.-diam wires, the data taken on 300-ratio wires show two clearly defined annealing stages for both 5- and 30-min anneals.

Some typical isochronal-annealing curves for the various gold-tin alloys quenched from about 650°C are shown in Fig. 13. One of the annealing curves for the 300-ratio gold is included for comparison purposes. It should be noted that while only about 10% of the initial quenched-in resistance is still left in a 300-ratio gold wire annealed at 200°C, some 40 to 50% of the quenched-in resistance remains after a similar anneal in the gold-tin specimens.

Figure 14 shows the resistance left in, as a function of quenching temperature, for quenched wires which have been given an additional 5-min anneal at 200°C subsequent to the quench. For high-temperature quenches, such an anneal ought to allow the first two annealing stages to go to completion. Note that the fraction of the initial quenched-in resistance remaining after such an anneal is a decreasing function of the quench temperature, falling from about 80% for a quench from 300°C to 40 to 50% for a quench from 700°C.

Possible random and systematic errors associated with the resistance quenched into 0.016-in.diam pure gold wires were discussed in detail in the previous paper.[1] It was concluded that the observed scatter of

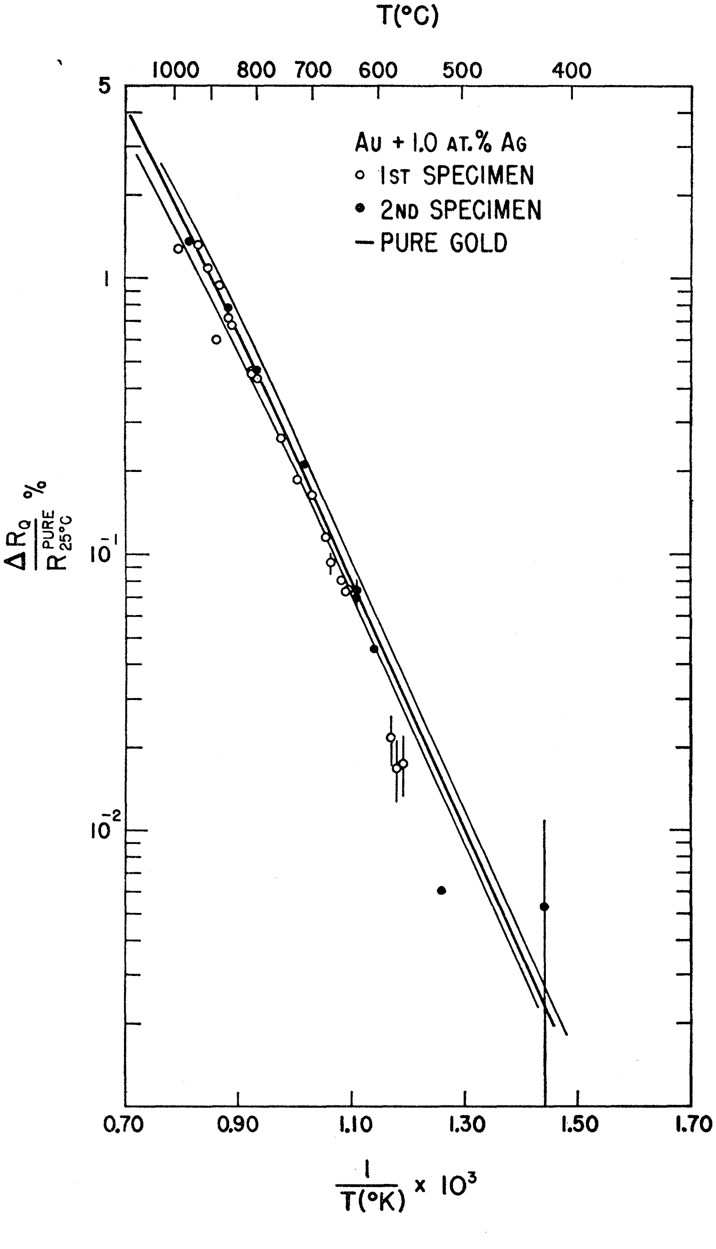

FIG. 8. The resistance quenched into gold-1.0 at.%-silver alloys compared to that quenched into pure gold.

the data was consistent with the expected random errors, and that systematic errors associated with the plunging of the hot wire into water were not crucial.

As the 0.002-in.-diam wires were quenched by turning off the heating current with the wire in helium gas or air, none of the problems associated with the 0.016-in.-diam wire being plunged into water occur. The quench temperature was that measured just prior to quenching, and possible quenching strains due to interaction between the wire and water were eliminated.

Two types of "cleansed" base were used for the 0.002-in. wires. The base obtained after the shorter anneal was reproducible to ±4.0 $\mu\Omega$ (0.2 μV with a current of 0.05 A; this corresponds to a resistivity of 2×10^{-11} Ωcm). The other base, obtained after a longer anneal, was not reproducible, but led to data which were in good agreement with those determined from the first type of base at high temperatures where the results were comparable. While the data taken from this second type of base were reproducible if two measurements from the same quench temperature were taken one right after the other, it was not possible to return to temperatures below 425°C after higher temperature quenches and still reproduce the quenched-in resistance originally obtained (see Fig. 4). It may well be that this low temperature nonreproducibility can be associated with the resistance not annealed out by 200°C after high temperature quenches (see Fig. 12). There is

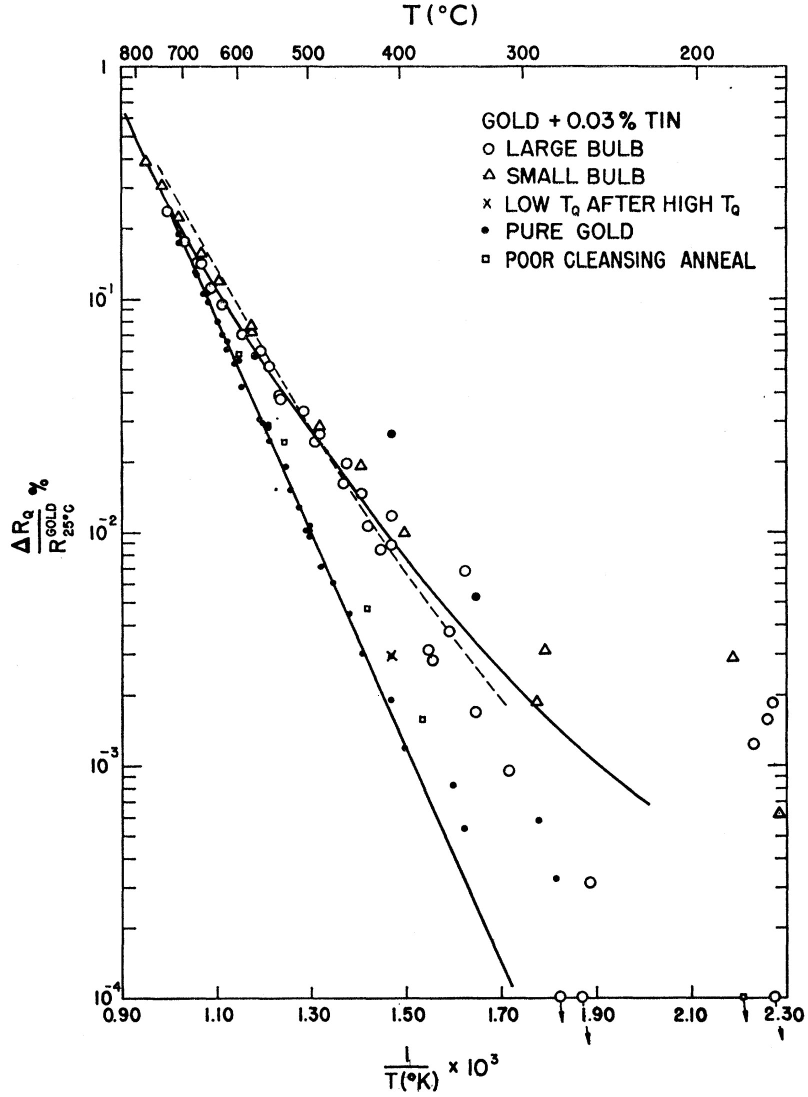

FIG. 9. The resistance quenched into gold-0.03 at.%-tin alloys compared to that quenched into pure gold.

no reason to believe that this lack of reproducibility means that the original low-temperature quench values were greatly in error. Nevertheless, it should be noted that the lack of reproducibility of the base, probably caused by specimen lengthening during the prolonged anneal, does leave open the question of whether all of residual vacancy clusters formed during previous quenches had been removed. The data determined for low temperatures by this technique should probably be considered as only lower limits for the quenched-in resistance from these temperatures.

Quenched-in resistances could not be measured on 0.002-in.-diam wires for quench temperatures greater than about 750°C because the wires developed instabilities causing them to burn out. The system was designed so that the wires usually burned through outside the gauge length. Data taken on the wire which burned through inside the gauge length were discarded as unreliable because of possible temperature inhomogeneity existing just before the burnout. Since the wires were examined for temperature uniformity while glowing before and after each quench series, this problem should not be a major source of error.

All errors, except those associated with the temperature scale and the reproducibility of the "cleansed" wire resistance at liquid-helium temperature, may be expected to be the same for both the 0.016-in.-diam gold-silver wires and the 0.016-in.-diam gold wires. The temperature scale used for gold-silver was discussed above, and is not apt to be a significant source of error.

For the gold-0.01 and 0.1 at.%-silver alloys the "cleansed" resistance at liquid-helium temperature was usually reproducible to better than ± 0.1 $\mu\Omega$ (0.1 μV with a current of 1 A; this corresponds to a resistivity change of 4×10^{-11} Ωcm). This is nearly as good as the reproducibility obtained for the pure gold wires.

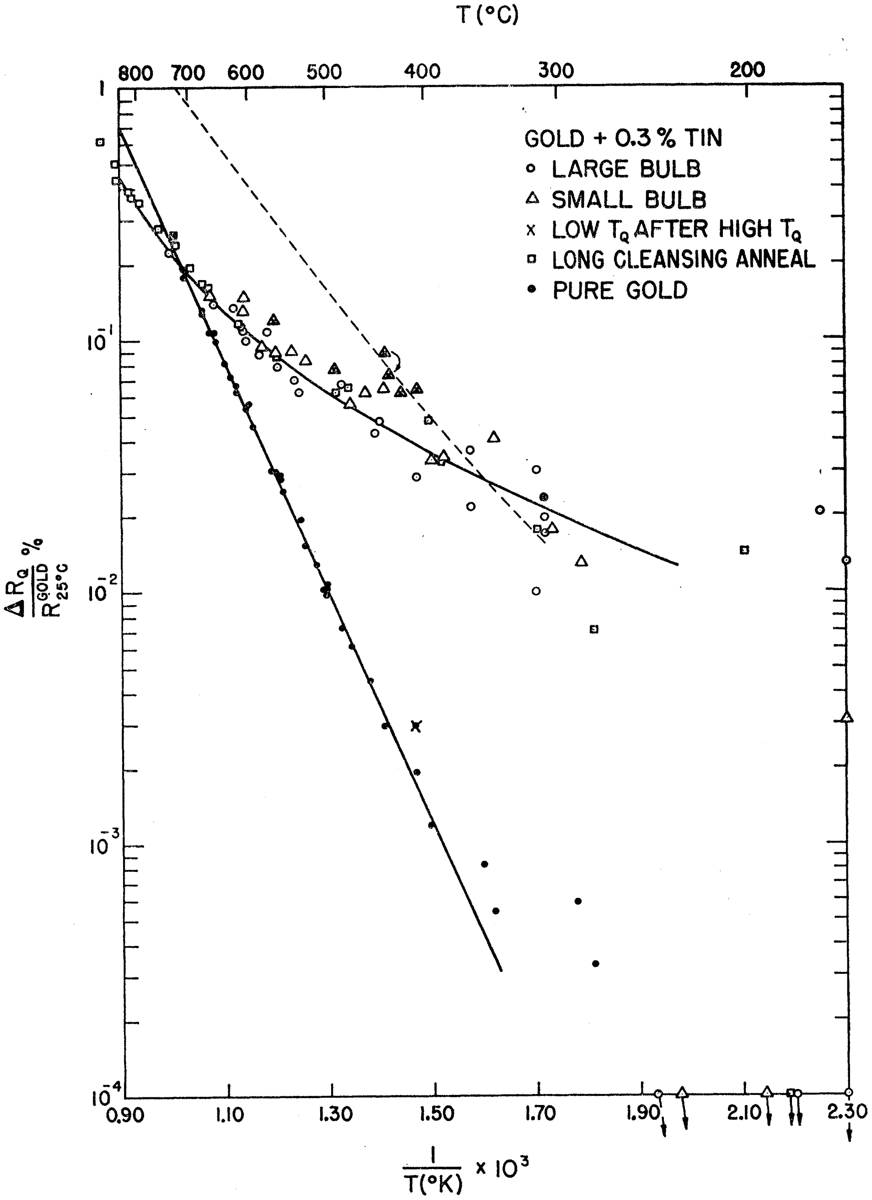

Fig. 10. The resistance quenched into gold-0.3 at.% alloys compared to that quenched into pure gold.

However, there was some difficulty in obtaining a satisfactory "cleansed" resistance for the gold–1.0%-silver alloys, particularly in the case of specimen No. 2. After the usual cleansing-anneal procedure described above, these wires were left overnight at room temperature. Quenches in the temperature range 200 to 500°C caused the resistance of the wire at liquid-helium temperature to decrease from the value obtained on the newly cleansed wire. The magnitude of this decrease seems too large to be explained as oxidation of the silver in the alloy, since the changes which occurred during subsequent quenches from low temperatures were usually substantially smaller than this initial decrease. The best estimates of the uncertainties to be assigned to the "cleansed" resistances are shown as error bars in Fig. 8. For the first specimen studied this represents an uncertainty of ±0.2 $\mu\Omega$, and for the second specimen an uncertainty of ±0.5 $\mu\Omega$.

Various errors may contribute to the uncertainty of the gold-tin data in addition to those already discussed for pure gold. The temperature rise at liquid-helium temperature of less than 0.2°C caused by the measuring current seems unlikely to be a significant source of error. The uncertainties associated with the determination of the quench temperature for the gold-tin alloys have been discussed.

No significant dependence of the quenched-in resistance on specimen bulb size was found for pure gold, nor,

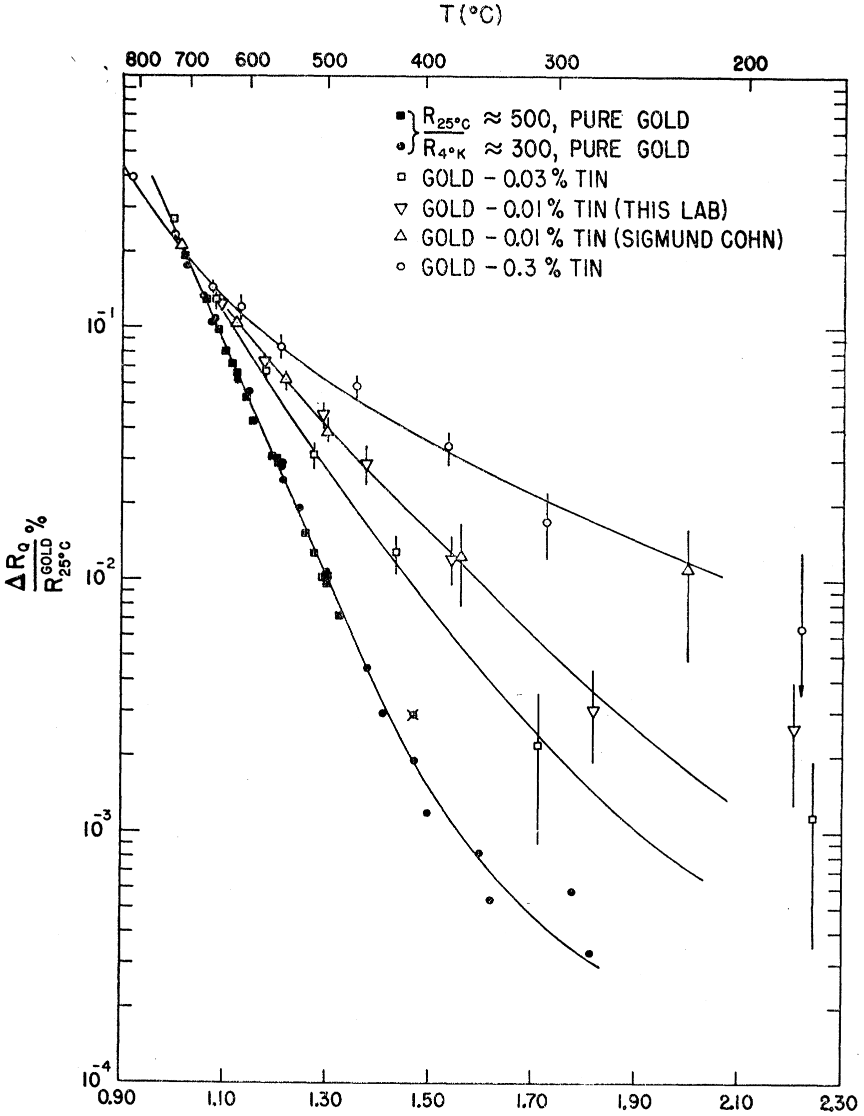

FIG. 11. Collected data for the resistance quenched into gold-tin alloys compared to that quenched into pure gold.

within the scatter of the data, was any effect found for the gold–0.1 and 0.3%-tin alloys. On the other hand, the gold–0.03%-tin alloys did show an effect possibly due to bulb size as shown in Fig. 9. It may be that a greater quench speed obtained in the smaller bulb, because of the greater pressure of the helium present, allows less clustering of "free" vacancies and tin impurities during the quench. This explanation is consistent with the pure gold and gold–0.03%-tin results, and while it would predict that a larger effect should be observed in the higher tin content alloys, the reproducibility of the data taken on these alloys may well not be sufficient to demonstrate such an effect.

Probably the major source of scatter in the gold-tin data is the difficulty found in obtaining a satisfactory "cleansed" resistance base. As previously noted, the base was not strictly reproducible from one cleansing anneal to the next. While this nonreproducibility was almost surely caused by the oxidation of a small fraction of the tin during the extended anneal, rather than by a slow removal of dislocations and vacancy clusters introduced during the drawing process, the effect was to leave an uncertainty about the presence of such dislocations and vacancy clusters after any given cleansing anneal. The existence of an isochronal annealing stage at high temperatures, as shown in Fig. 13, also added to this problem. Because of this uncertainty regarding the resistance base to be used, the resistance quenched into gold-tin alloys shown in Fig. 11 probably represents a minimum value for the actual quenched-in resistance, particularly at lower temperatures. However, in the absence of an understanding of all of the effects involved, all of the data have been treated equally and as though they represented all of the resistance to be

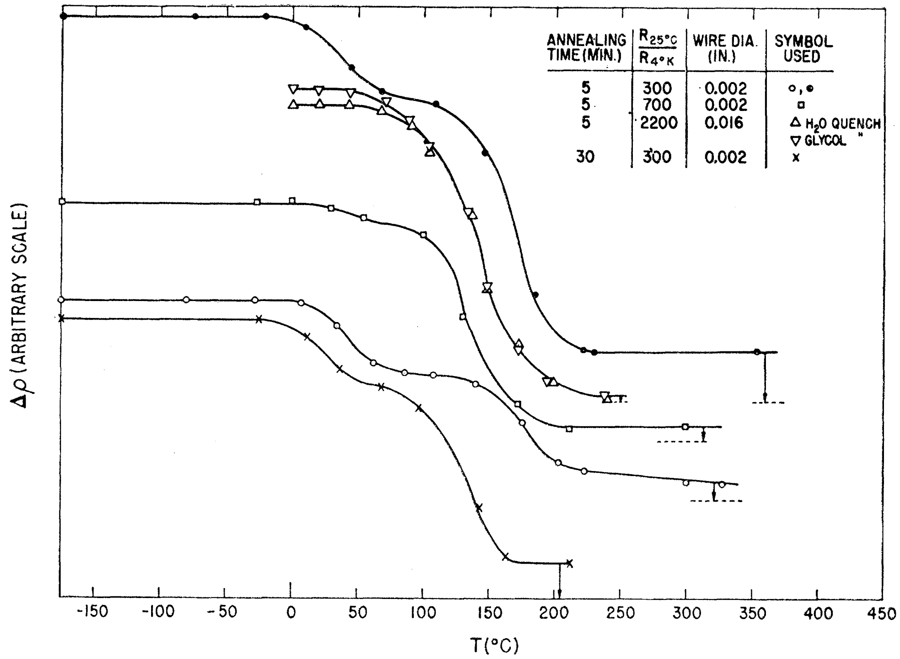

FIG. 12. Isochronal annealing data taken on two sizes of gold wire quenched from about 650°C.

quenched in. Since the error to be associated with each point is brought out clearly from the scatter of the data at low temperatures, no error bars have been given for individual points.

IV. DISCUSSION

The fractional concentration of single vacancies $C_V{}^P(T)$ present at thermal equilibrium in pure gold at a temperature T can be written as

$$C_V{}^P(T)=\exp[-\Delta G_F{}^V/kT], \tag{1}$$

where T is the temperature in degrees Kelvin, k is the Boltzmann constant, and $\Delta G_F{}^V$ is the Gibb's free energy necessary to form a vacancy. If each vacancy has a resistance R_V, these vacancies produce a resistance of

$$R_V{}^P=R_V \exp[-\Delta G_F{}^V/kT]. \tag{2}$$

During a quench of finite duration in time, some of the vacancies present in thermal equilibrium will migrate to sinks, with a migration energy $\Delta G_m{}^V$, and be annihilated. By examining the dependence of the quenched-in resistance on quenching speed, information about both $\Delta G_F{}^V$ and $\Delta G_m{}^V$ can be obtained. In the previous paper,[1] the dependence upon quenching speed of the resistance retained in 0.016-in.-diam pure gold wires quenched into water, glycol and acetone, and in air was analyzed in terms of a theory developed by Flynn. For such wires the quenched-in resistance was shown to be reproducible over nine independent specimens, and to determine values of the enthalpies $\Delta H_F{}^V=0.98 \pm 0.02$ eV and $\Delta H_m{}^V=0.83\pm0.04$ eV. The actual resistance loss observed for various quench temperatures and quenching speeds was equivalent to that expected for wires with a grain diameter of about 0.001 in., much smaller than the observed grain size of 0.005±0.001 in. It was noted that the quenching speeds presently available do not seem to allow all of the equilibrium number of vacancies to be retained in 0.016-in.-diam gold wires during quenches from above 600°C.

Figures 4 and 5 show that, where the data are comparable, the resistance quenched into 0.002-in.-diam gold wires agrees well with that quenched into 0.006-in.-diam wires. In addition, Fig. 12 shows that the isochronal annealing behavior of sufficiently pure 0.002-in.-diam gold wires is essentially the same as that for pure 0.016-in.-diam gold wires. Because the grain size of the smaller wire is still sufficiently large to account for the vacancy loss data taken on the 0.016-in.-diam wires, there is no inconsistency in this agreement. Rather, the agreement appears to strengthen the conclusions of the previous paper.

In particular, the agreement between the resistance quenched into the 0.002-in.-diam wires with that quenched into the 0.016-in.-diam wires in the vicinity of 500°C is heartening, since at these temperatures nearly all of the equilibrium vacancy concentration should be retained during the quench. Values of quenched-in resistance in the purest 0.002-in.-diam gold specimens for quench temperatures below 500°C are also consistent with a value of 0.98 eV for $\Delta H_F{}^V$. However, because of the relatively large errors associated with these very low-temperature measurements, these points cannot be considered as more than corroborative.

The reason for the difference between the isochronal annealing curves for 0.002-in.-diam gold wires of resistance ratio $(R_{25°C}/R_{4°K})$ equal to 300 and 700, respec-

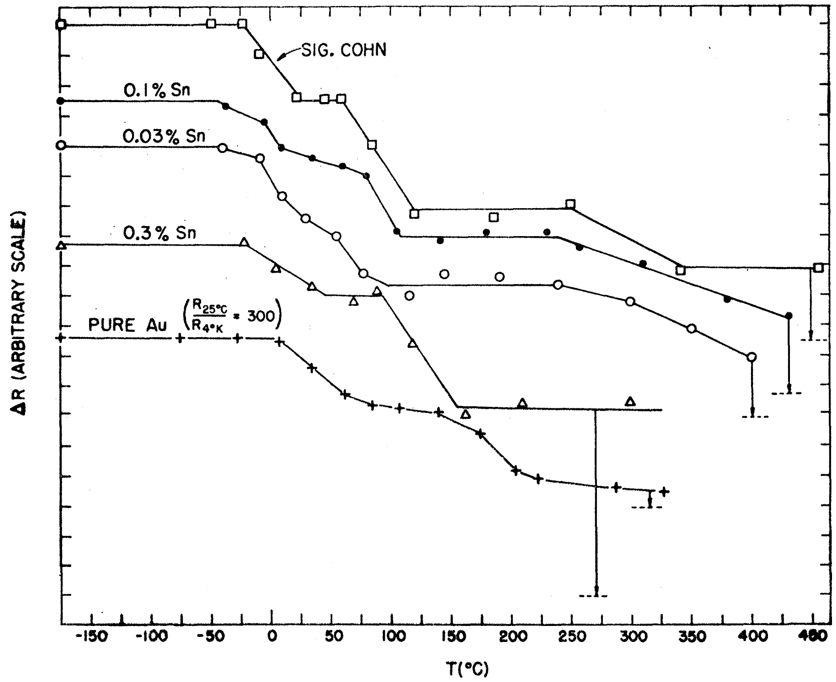

FIG. 13. Typical isochronal annealing curves for gold-tin alloys quenched from about 650°C.

tively, is not understood. It appears as though a new, low-temperature annealing stage occurs in the 300-ratio specimens and that the high-temperature annealing stage shifts to a higher temperature. Since the 300-ratio specimens had been baked out and had been in the same bulb with a tantalum getter which was heated in vacuum to 2100°C, impurities introduced during these operations may account for the differences observed. It also appears that the resistance quenched into these specimens at low temperatures is somewhat higher than that quenched into the purer 700-ratio specimen. While the origin of these differences is not clear, they probably arise from effects caused by nongaseous impurities. All of the specimens were quenched in pure helium containing only a few parts per million of other gases, and so should have the same gaseous background, except for those residual gases removed from the bulb containing the 300-ratio specimens by the gettering procedure.

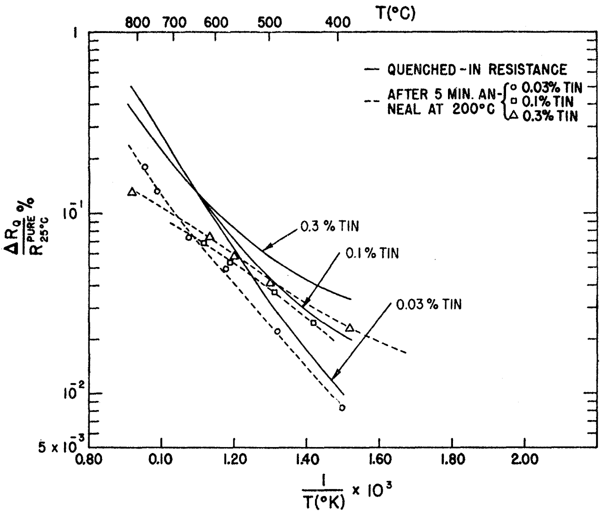

FIG. 14. Resistance remaining in quenched wires which have been given a 5 min anneal at 200°C subsequent to the quench.

On the basis of the data presented in the previous paper and above, it appears reasonable to assume that the resistance quenched into the two sizes of gold wires studied is a satisfactory measure of the equilibrium vacancy content of the wires at the quench temperature, and may be used as a base against which to compare the resistance quenched into dilute alloys.

According to the model suggested by Seitz,[23] and developed by Lidiard,[24] the thermal equilibrium concentration of vacancies, $C_V^I(T)$, in a dilute alloy with face centered cubic structure at an absolute temperature T, can be expressed as

$$C_V^I(T)=C_V^P(T)[(1-12C_I)+12C_I\exp(B/kT)], \quad (3)$$

where $C_V^P(T)$ is the concentration of vacancies at T in the pure metal [see Eq. (1)]; B is the binding energy between a vacancy and an impurity; and C_I is the concentration of impurities.

This model is based on the following assumptions: The impurity is randomly distributed in solution at only a small fraction of the total lattice sites; the interaction between a vacancy and an impurity extends only to

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[23] F. Seitz, Acta. Cryst. 3, 355 (1950).

[24] A. B. Lidiard, Phil. Mag. 5, 1171 (1960).

nearest-neighbor positions, and can be described in terms of a binding energy between the vacancy and the impurity; interactions between vacancy clusters and impurities may be neglected. This model has been the basis for the theoretical analysis of essentially all the studies of point defects in alloys that have been reported.

If the thermal equilibrium distribution of vacancies could be preserved during a quench, the resistance $R_V{}^I(T)$ associated with the quenched in vacancies would be, from Eq. (3),

$$R_V{}^I(T)=R_V{}^P(T)[(1-12C_I)+12C_I\Delta\exp(B/kT)], \quad (4)$$

where

$R(T)=$ resistance quenched into the pure metal,

$\Delta=1-[((r_V+r_I)-r_{V-I}/r_V)]$,

$r_V=$ resistance of 1 at.% of vacancies,

$r_I=$ resistance of 1 at.% of impurities,

$r_{V-I}=$ resistance of 1 at.% of vacancy-impurity pairs.

It is clear that to describe an actual quench, two possible effects must be considered in even the simplest alloys, namely, vacancy loss to sinks during the quench, and the pairing of initially "free" vacancies and impurities during the quench.

Korevaar[25] and Asimow[9] have suggested another possible means for obtaining a quenched-in resistance. They note that if the alloy shows a temperature-dependent short-range ordering, and if the ordered and disordered states have different resistances, a quenched-in resistance can be obtained even in the absence of vacancies.

Measurements of the diffusion coefficients for silver in gold, for silver in gold-silver alloys with more than 50% gold, and for gold-silver alloys with more than 50% gold,[26] show that in no case do the activation energies found differ from the activation energy for self-diffusion in gold by more than 0.16 eV. This result suggests a small binding energy between a silver impurity and a vacancy in gold. The calculations of LeClaire,[5] which fit the silver in gold-diffusion data in a satisfactory manner, suggest a binding energy between a vacancy and a silver atom in gold of about 0.02 eV.

The data of Fig. 7, showing no difference between the resistance quenched into pure gold and gold-0.01 and 0.1 at.%-silver alloys are consistent with a low vacancy-silver binding energy in gold. In fact, if the assumptions are made that the resistance of a paired vacancy-silver atom is the same as the resistance of a separated vacancy and silver atom, as well as that the entropy change associated with the pairing is small, the data and Eq. (4) determine a binding energy of less than 0.15 eV (the dashed line on Fig. 7 is drawn for a binding energy of 0.25 eV). Both of these assumptions are consistent with present knowledge, which unfortunately is small. However, it should be noted that the agreement between the two sets of data could be caused by a fortuitous combination of a small vacancy-impurity resistance when paired and a higher binding energy between a vacancy and a silver atom. This experimental technique does not allow an unambiguous interpretation of the data.

Because of the uncertain nature of the low-temperature data taken on the gold-1.0 at.%-silver alloys, no great amount of additional information can be gained concerning the vacancy-silver binding energy. However, the agreement between the resistances quenched into pure gold and the gold-1.0% silver alloys at high temperatures is consistent with the above conclusions.

Although the scatter of the data is sufficient to preclude a definite conclusion, it is tempting to assume that the effect noted by Asimow,[9] in which the resistance quenched into a gold-3.0 at.%-alloy showed a minimum as a function of temperature, is also evident in the gold-1.0%-silver data of Fig. 8. This assumption, that the decrease of quenched-in resistance relative to that found for pure gold is real, would help to explain the surprisingly high value for $\Delta H_F{}^V$ reported by Kloske and Kauffman[18] for quenching experiments of a gold -1.0 at.%-silver alloy. If their low-temperature points were substantially lower than those for pure gold, they would obtain an anomalously high $\Delta H_F{}^V$. Whether or not this interpretation is correct, the problems raised serve to point out the difficulties associated with attempts to determine a binding energy between vacancies and impurities from data taken on only one alloy concentration, from data taken on alloys with too large an impurity concentration, or from data taken on alloys without comparable data, taken in the same laboratory, on the pure material.

The theory of Lazarus[3] predicts a binding energy between a vacancy and a tin atom in gold of about 0.06 eV, while that developed by Flynn[6] predicts about 0.17 eV. The diffusion data taken for tin diffusing into silver,[27] a system which should be similar to tin in gold, show that the activation energy for the diffusion of tin in silver is less than the activation energy for self-diffusion by 0.21 eV. LeClaire[4] has shown that a modified version of the Lazarus theory gives a prediction in good agreement with this change. The above suggests that the binding energy between a vacancy and a tin atom in gold is less than 0.2 eV. With this in mind, we consider the present data.

The experimental observations to be explained are the following:

(1) The resistance quenched into dilute gold-tin alloys, as a function of quenching temperature is shown in Fig. 11. For low-temperature quenches, the quenched-in resistance is much larger than that quenched into pure gold, and at temperatures in the vicinity of 300°C it appears to increase roughly linearly with impurity con-

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[25] B. M. Korevaar, Acta Met. **6**, 572 (1958).

[26] W. C. Mallard, A. B. Gardner, R. F. Bass, and L. M. Slifkin, Phys. Rev. **129**, 617 (1963).

[27] C. T. Tomizuka and L. O. Slifkin, Phys. Rev. **96**, 610 (1954).

centration. As the quenching temperature is increased, the resistance quenched into the alloys approaches that quenched into pure gold, until at temperatures near 750°C, the alloy resistance becomes indistinguishable from the pure-gold resistance for the two lowest tin concentrations, and actually appears to become less than the pure-gold resistance for the gold–0.3% alloy.

(2) Quenches from the same temperature, taken immediately after an initial quench, give the same quenched-in resistance as the initial quench within experimental error. Low-temperature quenches taken subsequent to high-temperature quenches show quenched-in resistances that are higher than the values measured during the initial ascending temperature measuring series for quench temperatures less than 450°C, but are the same, within experimental error, for similar quenches from higher temperatures.

(3) A 5-min anneal at 200°C causes only about 20% of the initial quenched-in resistance to disappear after quenches from temperatures near 300°C, but the fraction lost increases with increasing quench temperature until 50 to 60% of the resistance quenched in from about 700°C is lost during such an anneal (see Fig. 14).

(4) Isochronal annealing measurements of the temperatures at which the quenched-in resistance anneals out of gold-tin alloys quenched from about 650°C show activated processes in three temperature ranges.

All of these observations cannot be described solely in terms of the simple model used to obtain Eq. (4). This equation predicts that the difference between the resistance quenched into the alloys and that quenched into pure gold should increase linearly with impurity concentration at all temperatures, a conclusion in disagreement with the data of Fig. 11. Nor does this model permit any simple explanation for the nonreproducibility of data taken for low-temperature quenches subsequent to high-temperature quenches, or for the temperature dependence of the large amount of resistance remaining after a 200°C anneal as described in point 3 above. In addition, no values for the change in resistance of a vacancy next to an impurity Δ can be found which allow the data to be reconciled with a vacancy-tin binding energy of less than 0.2 eV, as suggested by the diffusion measurements and calculations noted above.

If Eq. (4) is modified by allowing either a greater vacancy loss during the quench for the alloys than occurs in pure gold, or by considering the effect of clustering of vacancies and tin atoms into pairs during the quench, only the requirement of a linear concentration dependence of the quenched-in resistance would be modified. The other problems would not be solved. Since the annealing curve for the gold-tin alloys shows only one minor annealing stage occurring at lower temperatures than the annealing stage for the purest gold specimens, it seems unlikely that a considerably larger fraction of the equilibrium vacancy concentration will be lost during the quench for such alloys than for pure gold. It should be noted that the vacancy loss for pure gold, in the temperature range of interest for the alloys, is expected to be less than 20% on the basis of the data and theory presented in the previous paper.[1] While the assumption of vacancy-impurity pairing during the quench is entirely reasonable, and is in fact required for binding energies larger than 0.2 eV, it is not sufficient to allow all of the data to fit a modified version of Eq. (4).

The possibility that some qualitative difference exists between the data taken on the 0.03%-tin alloy and that taken on the 0.3%-tin alloy seems remote. All four of the experimental observations noted above apply equally to each tin concentration. Nevertheless, as a cautionary note, it should be mentioned that if only a single specimen had to be considered, for example the gold–0.03%-tin alloy, the quenched-in resistance for this one alloy could be described by Eq. (4) over a considerable temperature range. The dashed curve on Fig. 9 represents such a fit with $B=0.4$ eV and $\Delta=1$. This curve fits the data up to a temperature near 600°C, and by assuming Δ just a bit smaller than one, and correcting for vacancy-tin pairing during the quench, a binding energy a little larger than 0.4 eV can probably be used to fit the data in a satisfactory manner. This apparently spurious agreement shows the difficulties associated with attempting to interpret data taken on only one alloy concentration or over a restricted temperature range. In order to show the disagreement between this set of assumptions and the full set of data, a similar dashed curved is drawn on Fig. 10 for the gold–0.3%-tin alloy. Here the curve is quite inconsistent with the data.

Since this simple model is not sufficient to describe the present data, we might consider other possible influences than those considered in the derivation of Eq. (4).

Any additional variables introduced, such as by allowing the presence of larger vacancy-impurity clusters of two or more vacancies bound to an impurity or two or more impurities bound to a vacancy, permit sufficient lattitude that the data of Fig. 11 can probably be satisfactorily described. However, there appears to be no way in which all of the parameters in a more complex model can be uniquely defined in terms of the present results. Nevertheless, it may be useful to consider some possible qualitative explanations for the data.

The fact that the nonreproducibility of the low-temperature quench data taken subsequent to high-temperature quenches is evident also in pure gold specimens (see Fig. 4), as well as in the gold-tin specimens, suggests that the effect may be due to the formation of small vacancy-impurity clusters with sufficient stability to preclude their breaking up at temperatures less than 450°C. Not enough information is available for pure gold to determine if a small vacancy cluster could be sufficiently stable to cause this effect. Unfortunately, the temperature dependence of the loss of quenched-in resistance during an anneal of 5 min at 200°C, as shown in Fig. 14, is not easily understood simply in terms of such clusters. It is difficult to specify conditions under which a large fraction of the vacancies present after a low-temperature quench would cluster which would not similarly affect the larger number of vacancies present after a high-temperature quench. With any simple model, one would not expect a larger initial concentration of vacnacies to lead to a smaller fraction of the vacancies forming clusters.

The existence of a temperature-dependent short-range ordering among the tin atoms may be invoked to explain the large amount of resistance quenched into the alloys at low temperatures. If the ordering and the resistance of the ordered and disordered states were such as to give an increase in resistance with temperature, the data of Fig. 11 might be reconciled with a small vacancy-impurity binding energy. However, a calculation of the average number of jumps made by a tin atom in 5 min at 200°C, using the measured diffusion coefficient for tin in silver as a rough estimate, shows that a tin atom can make about one jump under these conditions. Because the quenched wire is apt to contain more vacancies than the same wire at thermal equilibrium, this calculation will tend to underestimate the number of jumps made. Since the tin atoms will be able to move during this anneal, it seems as though the ordered state will not be preserved. Although this model comes the closest to a reasonable explanation of the data, it too does not appear quite sufficient in all respects.

It appears as though an explanation of all of the above points can be made in terms of the following model: a moderate vacancy-tin binding energy (i.e., $B \leqslant 0.2$ eV) and a paired resistance which is less than the separated vacancy and tin resistances (i.e., $\Delta \leqslant 1$); the formation of small vacancy-impurity clusters as described above; and a short-range ordering which is stable against a single impurity jump. However, because of the speculative nature and complexity of this model, further discussion does not appear warranted.

It should be noted in conclusion that while most authors have interpreted data taken on dilute alloys in terms of a simple vacancy-impurity binding energy, few have shown that this model is satisfactory. Because of the problems outlined above, binding energies determined without sufficient experimental proof that the model gives a valid description of the data must be treated with caution.

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