

Calorimetric Studies on Annealing Quenched-In Defects in Gold

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Energy evolved on annealing quenched-in defects in gold has been measured with a high-precision, fast-adiabatic microcalorimeter. The energy can be described by an equation, $\Delta E_T = B \exp(-E_f/kT_Q)$, where ΔE_T is the total energy evolved for a quench from temperature, T_Q . B is a constant equal to $(4.5 \pm 1.0) \times 10^4$ cal/g-atom. E_f , the energy of formation of the defect, is equal to 0.97 ± 0.1 ev in good agreement with the value reported by Bauerle and Koehler from resistometric studies. The activation energy of motion of the defects has a temperature dependence confirming the results obtained resistometrically, i.e., $E_m = 0.73$ and 0.62 ev at $T_Q = 820^\circ\text{C}$ and 920°C , respectively. Assuming that the quenched-in defects are single vacancies, the energy measurements can be combined with the resistivity data of Bauerle and Koehler to give the resistivity increase per one atomic percent vacancies, $\Delta\rho_0/\Delta E_T/E_f$, using only experimentally derived quantities. This ratio equals 1.80 ± 0.6 $\mu\text{ohm cm/at. \%}$. The volume increase of the gold lattice per vacancy determined from the ratio, $\Delta\rho_0/\Delta E_T/E_f$, and Bauerle and Koehler's relationship between resistivity and fractional volume change during recovery, is 0.57 ± 0.05 in good agreement with recent theoretical work of Tewordt.

INTRODUCTION

DURING the past several years much effort has been directed to the study of structural defects in metals. An important phase of this work has been investigations concerned with lattice imperfections, in equilibrium at some high temperature, and retained upon rapidly cooling the metal. The presence of these defects is accompanied by an increase in resistivity,¹ and an increase in volume.¹ Because of its relative simplicity, the resistometric technique has by far received the most attention. [For example see the bibliography of reference 1.] The interpretation of the results observed and obtained by this method, including recovery kinetic data, in terms of lattice vacancies appears to be the most straight-forward.² However, factors giving rise to the increase in resistance upon rapid quenching and subsequent anneal may not always be uniquely due to the quenched-in imperfection *per se* but to other factors as well. For example, rearrangement of atoms during the annealing process can influence the scattering probability of the conducting electrons in addition to that caused by the defects themselves. Such inherent difficulties in the corresponding theoretical interpretation of the resistivity results could make such a study an indirect one. For this reason other studies such as volume change during recovery¹ have supplemented the results obtained from the resistometric technique.

A fundamental measurement would be that of determining the energy released (or change in internal energy) effected by annealing out of the quenched-in imperfections. In the formation of a defect, energy is stored in the lattice; it is released in the form of heat upon annihilation of the defect. Such basic information would further contribute to the understanding of the defects and their annealing behavior. For example, if there is good correlation between the results obtained

from the resistometric and from the calorimetric studies (such as agreement in the determination of the activation energies of formation and motion as well as in the kinetic data), then both studies combined with volume change data on the annealing of imperfections in the lattice could lead to a direct experimental evaluation of (1) the change in resistivity per atomic percent vacancies (heretofore, this number has been based entirely on theoretical considerations), (2) the change in volume of the crystal per vacancy.

Some preliminary results on the energy released upon annealing quenched-in defects in gold have recently been reported by us.³ Since then, the calorimeter has been modified, improved and the earlier measurements extended. A description of the calorimeter and the new results are reported here. These include the evaluation from the data of (a) the activation energy of formation of the defect (E_f), (b) the activation energy of motion of the defect (E_m), (c) kinetic behavior on recovery, (d) the change in resistivity per one atomic percent vacancies, and (e) the increase in volume of the lattice per vacancy. The information presented in (d) and (e) has been obtained by combining some of the calorimetric data with Bauerle and Koehler's results¹ on variations in the electrical resistance and volume change observed during the recovery of quenched-in imperfections in gold.

EXPERIMENTAL

Calorimeter

The adiabatic microcalorimeter is a modification of one used earlier.⁴ It is presented schematically in Fig. 1. The important new feature compared to the previous design is the introduction of a "storage" chamber, for the sample in addition to the "annealing" chamber.

³ W. DeSorbo, Phys. Rev. Letters **1**, 238 (1958).

⁴ W. DeSorbo, Twelfth Annual Calorimetry Conference, Portsmouth, New Hampshire, September 3-7, 1957 (unpublished); see also DeSorbo, Treafis, and Turnbull, Acta Met. **6**, 401 (1958).

¹ J. E. Bauerle and J. S. Koehler, Phys. Rev. **107**, 1493 (1957).

² Koehler, Seitz, and Bauerle, Phys. Rev. **107**, 1499 (1957).

The specimen, after having been quenched and transferred to the storage chamber without any loss of quenched-in defects (see below "procedure"), can be kept indefinitely in the calorimeter without permitting recovery to take place. Being able to thus "preserve" the specimen inside the calorimeter prior to the measurements, permits (a) the assembly of the various auxiliary parts of the apparatus, (b) the evacuation of the unit to better than 10^{-5} mm of Hg, (c) the stabilization of the various instruments, and (d) the adjustment and control of the background temperature for the calorimeter container. Once these steps have been taken, the calorimeter container which serves as a fast adiabatic jacket for the sample, is rapidly raised from the lower chamber (maintained at a temperature low enough to prevent recovery) to the upper chamber where temperature has been preset to that at which annealing is to take place. The temperature of the container and specimen can be rapidly adjusted to that of the new environment. The measurement of energy release due the quenched-in imperfections can then be commenced. This experimental procedure has significantly reduced the time interval between the start of the annealing reaction and the time of first measurement. The accuracy of the final results have thereby been improved, especially in those experiments where the sample is quenched from relatively higher temperatures ($T_q > 875^\circ\text{C}$).

The "storage" chamber is situated in the lower copper block where temperature can be controlled externally by surrounding the lower copper rod and fins (see Fig. 1) with an appropriate cold-bath (such as dry-ice acetone mixture). The "annealing" chamber is located in the upper massive copper block which is removable to permit the transfer of the sample to and from the storage chamber. The two chambers are connected by a brass cylinder and a number of insulating spacers all of which permit the calorimeter container to move in an upward or downward direction. The temperature of the upper copper block is adjusted to that which is desirable to carry on the annealing studies during the experiment (T_a). This background temperature is controlled automatically to $\pm 1 \mu\text{v}$; and is accomplished by balancing the emf of a copper-constantan thermocouple with a White potentiometer (Leeds and Northrup, 10 000-1 μv range). Any small unbalanced signal from the potentiometer is amplified by a Liston-Becker dc amplifier. A Leeds and Northrup type H recorder controller serves as a null point indicator. A microswitch in the recorder, responding to unbalances of less than 1 μv , turns the circuit "on" and "off" for one of the two similar heaters wound non-inductively around the upper copper block. Steady current is adjusted through the second heater.

The calorimeter container consists of a copper can, $1\frac{1}{2}$ -in. outer diameter, $\frac{1}{8}$ -in. wall (except in the regions for screw threads), and $2\frac{1}{2}$ in. high. Two heater wires are wound noninductively on machined grooves around

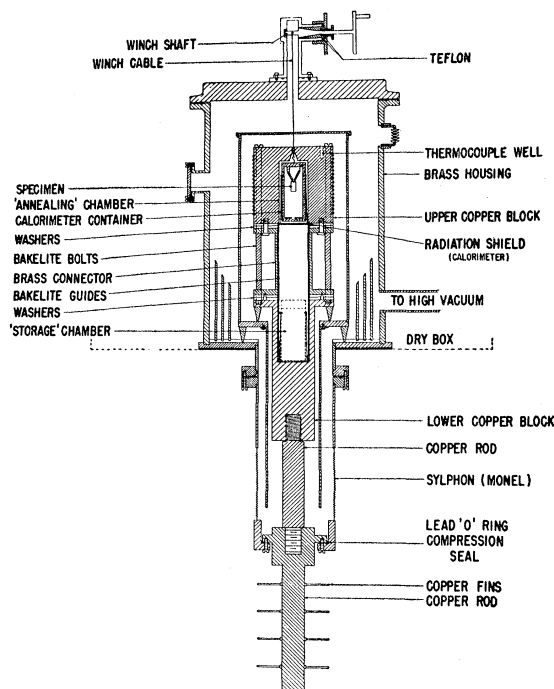


FIG. 1. The adiabatic microcalorimeter with both specimen "storage" and "annealing" chambers.

the outer wall. The top is fitted with a removable copper cap that makes good thermal contact with the container cylinder by machined surfaces and a compression seal effected by three copper screws.

Specimen

The gold samples consisted of rectangular slabs $\frac{1}{2}$ in. $\times \frac{3}{16}$ in. $\times 0.015$ in. rolled from an approximately $\frac{1}{8}$ -in. diameter rod obtained from Sigmund Cohn Corporation, Mount Vernon, New York. This stock was listed by them as "chemically pure, 99.999%." An emission spectroscopic analysis carried out by L. B. Bronk of our laboratory listed the following impurities present in "trace" amount: Cu, Fe, Mg, and Si; not detected were Pb, Sn, Bi, Ag, Pt, Ni, Co, Mn, Zn, In, Ca, Sb, Ti, Li, Tl. The residual resistivity ratio, $R_{273^\circ\text{K}}/R_{4.2^\circ\text{K}}$, determined for a wire specimen drawn to 0.016 in. from the original $\frac{1}{8}$ -in. stock and then annealed, was found by us to be 1572. The fine chromel-alumel leads (0.002-in. diameter) comprising the difference thermocouple were attached mechanically to the top side of the gold sample. A small hole of sufficient radius and depth was drilled to just accommodate the thermocouple junction. Good thermal contact was made between the sample and the thermocouple by deforming a small region of the metal around the junction. This type of connection resulted in a lower electrical background noise level (thermal) than that observed when the junction was spot welded to the specimen.

Homogenization

The sample, with the difference thermocouple attached to it, was heated, prior to the quench, in a furnace arrangement described by Turnbull *et al.*⁵ Calibrated oscillograph camera records showed the quenching rates, using ice-water mixture as a quenching medium, to vary from 0.8×10^4 to 1.1×10^4 °C/sec. These oscillograph studies also provided a means for correcting the slight drop in temperature of the sample just before submersion in the quenching solution. Immediately after quench, the sample was dried by rinsing it, successively, in alcohol and in ether (each at temperatures below -40°C), then stored in liquid nitrogen.

Procedure

With the sample still submerged in liquid nitrogen, one lead of the difference thermocouple, alumel, was soldered directly to bottom side of the removal cap of the calorimeter; while the chromel wire was soldered to an insulated pin that was in good thermal contact with the cap. These leads also served to support the sample. The cap with the sample thus attached was transferred to the dry box, and subsequently positioned and fastened with copper screws to the top of the calorimeter container located in the storage chamber. This procedure was effected with the sample submerged in liquid nitrogen to prevent any recovery.

To start the annealing reaction the calorimeter container and cap with suspended sample was rapidly raised by a winch mechanism, guided by bakelite tracks from the lower chamber to the upper one. The strain-free thermocouple (soldered in a thermocouple well situated at the lower side of the calorimeter container) and other electrical lead wires were guided by a slit cut vertically along the brass connector and washers (see Fig. 1). During this lifting operation, current was simultaneously turned on for each of the two heaters of the calorimeter. The small mass of the container permitted it to be heated at rates of about 15–20 degrees per minute. Since the temperature difference between the calorimeter and the annealing chambers was not more than 50°C , the temperature of the former could be raised to the higher temperature in less than 3 minutes. During the lifting and heating operation of the container, the temperature of the specimen inside remained below that which any annealing could take place; the heat leak to the specimen during this short period of time was negligible. The sample could be readily heated to the appropriate annealing temperature in less than 60 seconds by passing a small current through the fine chromel-alumel difference thermocouple wires. The adjustment of the temperature of the sample and the calorimeter to within a temperature difference

of less than 10^{-3}°C could be attained in 3–5 minutes. The time (t_i) of first measurement of temperature rise due to the energy released in the sample could be accomplished in 5–10 minutes from the time of initial release of energy, t_0 . During the annealing reaction, the temperature difference between the specimen and the calorimeter container was kept less than $\pm 0.1 \mu\text{v}$ $\sim 2.0 \times 10^{-4}^\circ\text{C}$ by a semiautomatic control already described.⁴ The temperature of the annealing chamber was kept constant to $\pm 1 \mu\text{v}$ throughout the experiment as discussed above. The effectiveness of this chamber to provide a more uniform and constant background temperature for the calorimeter container was improved by the presence of a radiation shield that was spring-attached to the bottom of the container. The shield followed the calorimeter in its vertical or downward motion. When the calorimeter was in operating position (floating in the upper chamber), the shield broke contact with the bottom of the container but made good thermal contact with the copper block (see Fig. 1).

During the experiment the only measurement that was necessary was that of the temperature of the calorimeter as a function of time. Under the adiabatic conditions maintained between the specimen and its surrounding, the energy released would be a simple function of the temperature rise due to the heat evolved by the annihilation of the defects, i.e.,

$$Q_t = \left[\sum_{i=1}^{i=n} \bar{C}_{pi} \sum_{i=1}^{i=n} \bar{x}_i \right] \Delta T_t, \quad (1)$$

where ΔT_t = temperature rise at time t , \bar{C}_{pi} = heat capacity of component i , \bar{x}_i = No. of gram atoms of component i . The energy released from $t_i \rightarrow t$ in cal/g-atom of gold is

$$\Delta E(t) = Q_t / x_{Au}. \quad (2)$$

There were only two components making up the specimen, i.e., the gold slab and a portion of the fine chromel-alumel wires. Because of the small mass of the latter, correction due to these wires in Eq. (1) was practically nil. The data of Geballe and Giauque⁶ were used to derive the C_p values for gold in the temperature region of interest here.

The calorimeter temperature was determined by measuring the emf output of a strain-free copper-constantan thermocouple attached to the calorimeter. The thermocouple consisted of wires that had been tested and selected to give minimum extraneous thermal effects. The temperature emf calibration was based on the O.S.U. helium gas thermometer scale.⁷ The emf was measured with a 6-dial thermo-free Rubicon potentiometer and telescope galvanometer system that had a sensitivity of better than $200 \text{ mm}/\mu\text{v}$. The temperature rise, ΔT , due to the energy released in gold

⁵ D. Turnbull and H. N. Treafits, *Acta Met.* **3**, 43 (1955); see also Turnbull, Rosenbaum, and Treafits, *Acta Met.* (to be published).

⁶ T. H. Geballe and W. F. Giauque, *J. Am. Chem. Soc.* **74**, 2368 (1952).

⁷ Rubin, Johnston, and Altman, *J. Am. Chem. Soc.* **73**, 3401 (1951).

varied from about 0.45 degrees for the highest injection temperature (920°C) down to 0.18 degrees for the lowest (820°C) for time duration of 6-8 hours. This total rise in temperature could be measured to better than 10^{-3} °C. Any variations in electrical background noise, parasitic emf's, etc., that could influence the measurement of ΔT during the course of the run were corrected by determining the total of these small disturbances or "thermal," as a function of time, after completion of each run and under the same conditions as during the run.

RESULTS AND DISCUSSION

Figure 2 presents some typical results of the energy released in calories per gram atom as a function of time on annealing quenched-in defects in gold. The data are shown for various injection temperatures ranging from 920°C to 820°C, and for various annealing temperatures. Energy has been detected at injection temperatures as low as 770°C. However, at this temperature the precision was too low for the results to be significant. The total energy released for various injection temperatures is summarized in Table I. Other pertinent information necessary to evaluate the probable accuracy of the final results are also shown. The first column lists the injection temperatures and their probable error. An average error of $\pm 10^\circ\text{C}$ includes the uncertainty in (a) the calibration of the chromel-alumel thermocouple, (b) measuring the small drop in temperature of the sample after it leaves the furnace and before striking the quenching medium. The annealing temperature is the mean value of the initial and final temperature of the specimen ($T_a = T_i + \frac{1}{2}\Delta T$). The third column represents the energy evolved, $\Delta E]_{t_i}^{t_f}$, that has been measured experimentally between t_i , time of first measurement, and t_f , time of final measurement. The uncertainty in this measured quantity of the energy is less than 2%. The fourth column represents that portion of the energy released between zero time of the reaction and the time of first measurement, $\Delta E]_{t_0}^{t_i}$, which has been approximated by extrapolating and integrating to zero time the power data determined from the energy measured. The time interval of this extrapolation is approximately 10 minutes compared to 25-30 minute intervals encountered in the treatment of the data obtained with the earlier calorimeter (ref. cited). This

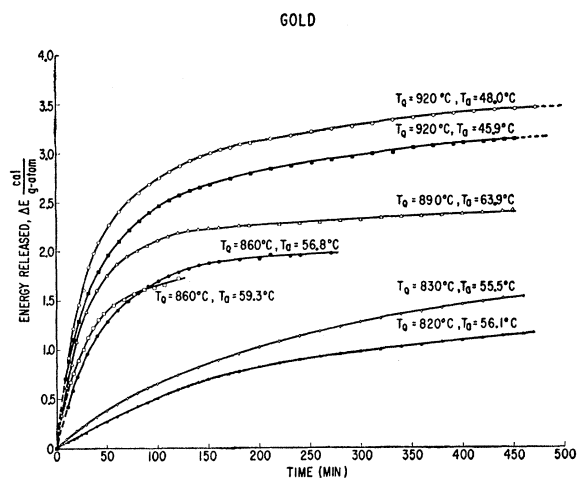


FIG. 2. Energy released (calories per gram-atom) during the annealing of quenched-in imperfections in gold at different injection and annealing temperatures (T_Q and T_A).

increment of energy, $(\Delta E]_{t_0}^{t_i})$, thus approximated amounts to about 20% of the total energy evolved for quenches from the higher temperatures ($T > 875^\circ\text{C}$) and less than 5% of the total energy evolved for quenches from lower temperatures and for the annealing temperatures reported here. The fifth column tabulates the portion of the energy, $\Delta E]_{t_f}^{t_a}$, approximated by a straight line extrapolation of the power curve beyond t_f . The slope of this line was the value of the power curve at t_f . This method undoubtedly yields a value of $\Delta E]_{t_f}^{t_a}$ somewhat smaller than the true value. This portion of the energy thus evaluated represents about 5% of the total energy evolved for the specimens quenched from higher temperatures increasing to about 15% for the lower injection temperatures. If these increments of energy, $\Delta E]_{t_0}^{t_i}$ and $\Delta E]_{t_f}^{t_a}$, have each been approximated to better than 50%, the over-all uncertainty in determining the total energy released for the temperature range reported is about 10-15%. The total energy evolved, ΔE_T , for various injection temperatures and the probable uncertainty in the value is shown in the sixth column.

Activation Energy of Formation E_f

Figure 3 shows a plot of the logarithm of the total increase in internal energy, ΔE_T , due to the "quenched-

TABLE I. Energy released on annealing quenched-in defects in gold.

$T_Q^\circ\text{C}$ (Injection temp.)	$T_a^\circ\text{C}$ (Annealing temp.)	$\Delta E]_{t_i}^{t_f}$ cal g-atom (Extrpl.)	$\Delta E]_{t_0}^{t_i}$ cal g-atom	$\Delta E]_{t_f}^{t_a}$ cal g-atom	ΔE_T cal g-atom
920 \pm 10	45.9	2.53	0.60	0.27, (452)	3.40 \pm 0.4
920 \pm 10	48.0	2.65	0.80	0.19, (492)	3.64 \pm 0.4
890 \pm 10	63.9	1.79	0.62	0.37, (450)	2.78 \pm 0.4
860 \pm 10	56.8	1.62	0.34	0.27, (241)	2.23 \pm 0.3
860 \pm 10	59.3	1.16	0.51	0.37, (125)	2.04 \pm 0.4
830 \pm 10	55.5	1.43	0.11	0.24, (460)	1.78 \pm 0.3
820 \pm 10	56.1	1.19	0.06	0.23, (470)	1.48 \pm 0.2

in" imperfections, as a function $1/T_Q$. The results can be described exponentially in the following manner:

$$\Delta E_T = 4.5 \times 10^4 \exp[-0.97/kT_Q] \text{ cal/g-atom}, \quad (3)$$

where k the Boltzmann constant and T_Q the injection temperature. It is inferred that the value 0.97 ev is the activation energy of formation of the defects, E_f .⁸ The value is in good agreement with that obtained by Bauerle and Koehler¹ from resistometric measurements.

Activation Energy of Motion, E_m

The activation energy of motion, E_m , can be calculated from recovery isotherms described by

$$\dot{\Delta E}'(t)/\Delta E'(t) = K \exp[-E_m/kT_a], \quad (4)$$

where $\Delta E'(t) = [\Delta E_T - \Delta E(t)]/\Delta E_T$, i.e., the fractional part of the stored energy remaining at any time t and $\dot{\Delta E}'(t) = d[\Delta E'(t)]/dt$. The more reliable method for determining E_m is that suggested by Kauffman and Koehler,⁹ where the term, $\dot{\Delta E}'(t)/\Delta E'(t)$ is evaluated immediately before and immediately after an abrupt change in the annealing temperature. Unfortunately, it is impractical with the calorimetric technique described above to follow this procedure. A second method that can be used is outlined in Fig. 4 where data for two different annealing isotherms are presented. If the concentration and distribution of dislocations is different for each quench, this method could lead to erroneous results. However, a study¹⁰ comparing these two methods for evaluating E_m in aluminum wires has shown good

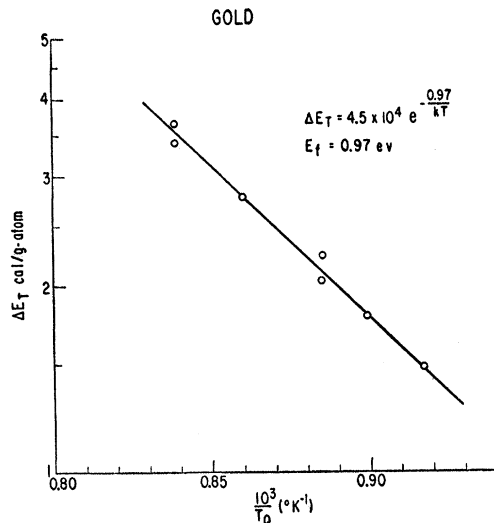


FIG. 3. Logarithm of total energy released (increase in internal energy), ΔE_T , due to the "quenched-in" imperfections, as a function of reciprocal temperature, T_Q , immediately before quench.

⁸ H. Brooks article on "Impurities and Imperfections" (American Society for Metals, Cleveland, 1955).

⁹ J. W. Kauffman and J. S. Koehler, Phys. Rev. **97**, 555 (1955).

¹⁰ W. DeSorbo and D. Turnbull, Phys. Rev. **115**, 560 (1959).

TABLE II. Activation energy of motion of quenched-in defects in gold.

$T_Q^{\circ}\text{C}$	T_{annealed}	E_m (ev)
920	45.90	0.6 ₂
	48.00	
890	50.52	0.6 ₄
	63.91	
820	56.10	0.7 ₃
	62.23	

agreement within the experimental uncertainty. The results obtained calorimetrically with this procedure for gold at three different temperatures are summarized in Table II. These results are in reasonable agreement with those reported by Bauerle and Koehler¹ from resistometric data and similarly show a dependence of E_m on T_Q . They report $E_m = 0.6_0$ ev for $T_Q = 1000^{\circ}\text{C}$ and $E_m = 0.8_2$ ev for $T_Q = 700^{\circ}\text{C}$.

Reaction Rates on Annealing Quenched-in Defects in Gold

Figure 5 presents plots of $\dot{\Delta E}'(t)/\Delta E'(t) = k'\dot{\Delta E}'(t)$ to compare the energy recovery rates for three different injection temperatures. For $T_Q = 860^{\circ}\text{C}$ and 820°C , the rates appear to consist of a first and second order component. For $T_a = 920^{\circ}\text{C}$, the rates could also include a first order component in addition to the second order but within the accuracy of the measurements this may not be too conclusive. In general, these results are consistent with the Koehler *et al.*² interpretation and similar to the resistivity recovery rates recently observed in aluminum.¹⁰

The Concentration of Vacancies, $C_v = \Delta E_T/E_f$

Assuming that the quenched-in defects are for the most part single vacancies² these calorimetric results can be used to determine the concentration of the defects based on experimentally derived quantities, ΔE_T and E_f . The values calculated for the various injection temperatures are tabulated in the third column of Table III. A comparison of these results with those deduced from resistometric^{2,11} and electron microscope transmission¹² studies is made in Table IV.

Since there is good correspondence in the results obtained resistometrically and those reported here, such as in E_f and E_m values, it is worthwhile to consider further information that can be deduced by combining some of the results of both investigations.¹³ The assumption that the quenched-in defects are for the most part single vacancies² is still adhered to.

¹¹ Kimura, Maddin, and Kuhlmann-Wilsdorf, Acta Met. **7**, 145 (1959); see also J. Metals **10**, 93 (1958).

¹² J. Silcox and P. B. Hirsch, Phil. Mag. **4**, 72 (1959).

¹³ Also note that samples used in the two experiments were furnished by the same supplier and were listed as having the same purity.

TABLE III. The resistivity increase per one atomic percent vacancies and the volume increase per vacancy-gold.

T_Q °K (Injection temp.)	ΔE_T —cal g-atom (Energy released)	$C_v = \frac{\Delta E_T}{E_f}$ ^a	$\Delta\rho_0$ $\mu\text{ohm-cm}^b$ (Resistivity increase)	$\frac{\Delta\rho}{\Delta E/E_f}$ $\mu\text{ohm-cm}$ at. %	$\frac{\Delta E_T}{\Delta\rho}$ cal g- $\mu\text{ohm-cm}$	χ (Volume inc./ vacancy)
1193	3.40	1.52×10^{-4}	2.89×10^{-2}	1.9 ₁	0.59 ₆	0.59 ₅
1193	3.64	1.63×10^{-4}	2.89×10^{-2}	1.7 ₈	0.63 ₁	0.55 ₆
1163	2.78	1.24×10^{-4}	2.26×10^{-2}	1.8 ₂	0.62 ₃	0.56 ₉
1133	2.23	9.97×10^{-5}	1.75×10^{-2}	1.7 ₅	0.64 ₇	0.54 ₈
1133	2.04	9.12×10^{-5}	1.75×10^{-2}	1.9 ₂	0.59 ₃	0.59 ₉
1103	1.78	7.96×10^{-5}	1.33×10^{-2}	1.6 ₇	0.67 ₉	0.52 ₂
1093	1.48	6.62×10^{-5}	1.21×10^{-2}	1.8 ₃	0.62 ₁	0.57 ₂
				av. 1.8 ₁	0.62 ₇	0.56 ₆

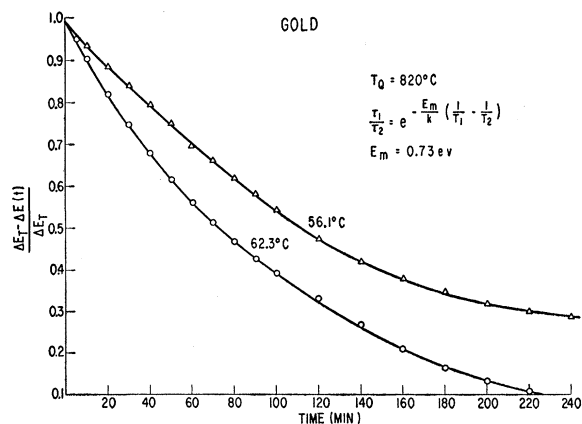
^a E_f evaluated calorimetrically = 0.97 eV.
^b $\Delta\rho_0 = Ae^{-0.98/kT}$; see reference 1.

Resistivity Increase per Atomic Percent Vacancies $(\Delta\rho_0/\Delta E_T)/E_f$

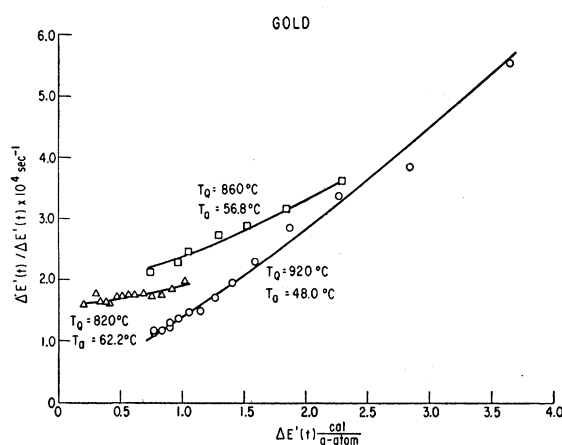
The calorimetric results, combined with the resistometric data of Bauerle and Koehler,¹ can be used to evaluate the ratio, resistivity increase per atomic percent vacancies, based entirely on experimentally derived quantities. Their resistometric results show that the total increase in resistivity due to quenched-in defects is related exponentially to the injection temperature, T_Q , i.e.,

$$\Delta\rho_0 = A \exp[-0.98/kT_Q]. \quad (5)$$

The fourth column of Table III summarizes $\Delta\rho_0$ values obtained from Eq. (5) based on $A = 4.0 \times 10^{-4}$ ohm-cm appropriate to T_Q and to our quenching rate of approximately 1×10^4 °C/sec. The value for the pre-exponential constant has been derived from extrapolating the variation of A with quenching rates reported by Bauerle and Koehler.¹ The change in resistivity ($\mu\text{ohm-cm}$) per atomic percent vacancies is presented in the fifth column. The average value is about 1.8 in good agreement with the more widely used theoretical value¹⁴ of

FIG. 4. Energy recovery isotherms for gold, $T_Q = 820^\circ\text{C}$.

¹⁴ P. Jongenberger, Appl. Sci. Research **B3**, 237 (1953); F. Abeles, Compt. rend. **237**, 796 (1953). F. J. Blatt, Phys. Rev. **103**, 1905 (1956); **99**, 1708 (1955).

FIG. 5. Comparison of energy recovery rates for different injection and annealing temperatures (T_Q and T_A).

about 1.5. The ratio shows no systematic trend with injection temperature within the experimental errors reported for both experiments.

Energy-Resistivity Ratio, $\Delta E_T/\Delta\rho_0$

The sixth column of Table III lists the ratio of the total energy released over the total change in resistivity for a given quench. The average value obtained is 0.63 cal/gram $\mu\text{ohm-cm}$. This value is to be compared with (a) the ratio $\Delta E/\Delta\rho_0 = 1.7$ cal/gram $\mu\text{ohm-cm}$ reported by Overhauser¹⁵ for copper irradiated by

TABLE IV. Concentration of quenched-in vacancies in gold determined by various methods.

T_Q °C	C_v	Method
920	1.5×10^{-4}	Calorimetric, this research
890	1.2×10^{-4}	Calorimetric, this research
900	2×10^{-4}	Resistometric ^a
900	8×10^{-5}	Resistometric ^b
900	6×10^{-5}	Electron microscope transmission ^c

^a See reference 2.

^b See reference 11.

^c See reference 12.

¹⁵ A. W. Overhauser, Phys. Rev. **94**, 1551 (1954).

deuterons; (b) the ratio, $\Delta E/\Delta\rho_0 = 3.0$ cal/gram $\mu\text{ohm-cm}$ determined from the results of Blewitt *et al.*¹⁶ on annealing copper irradiated by neutrons and (c) the stored energy-resistivity ratio of 5.4 cal/gram $\mu\text{ohm-cm}$ recently reported by Meechan and Sosin¹⁷ for copper irradiated by an electron beam.

Increase in Volume of the Crystal per Vacancy

Assuming isotropic dimensional changes in gold, Koehler *et al.*² have reported that the resistivity change ($\Delta\rho$) and the fractional change of volume $\Delta V/V$ on annealing quenched-in defects in gold can be related in the following manner:

$$\Delta\rho = K'\Delta V/V, \quad (6)$$

where experimentally $K' = 3.2 \times 10^{-4}$ ohm-cm.

If the volume of the lattice increases by one atomic volume when a vacancy is present, then the concentration of vacancies, $C_V = \Delta V/V$. However, if the increase in volume per vacancy is some fraction, χ , of the atomic volume, then

$$\chi = \Delta\rho/K'(\Delta E_T/E_f); \quad 0 < \chi < 1. \quad (7)$$

Equation (7) shows that increase in volume per vacancy referred to an atomic volume could be determined entirely from experimentally derived quantities: A summary of the results obtained in applying Eq. (7) to the data is presented in the last column of Table III. Within the experimental error reported, there appears to be no systematic variation of χ with T_Q . The average value of χ is 0.57 which compares favorably with the theoretical values of 0.47 and 0.55 reported by Tewordt¹⁸ and a value of 0.4 cited by Tucker and Sampson.¹⁹

Keyes²⁰ has recently reported a relationship between the activation volume, ΔV_a , and the activation energy of diffusion Q for some simple solids, i.e.,

$$V_a = k''\beta Q, \quad (8)$$

where k'' is a constant and β , the isothermal coefficient of compressibility. Except for sodium, most of the available experimental data were in reasonably good agreement with Eq. (8) when $k \cong 4$. It is interesting to point out that when this formula is applied to gold

with $\beta = 5.99 \times 10^{-13}$ cm⁻²/dyne²¹ and $Q = 1.8$ ev (i.e., $E_f \cong 1.0$ ev and $E_m \cong 0.8$ ev the latter considered more appropriate for single vacancies¹) then $\Delta V_a \cong 4.2$ cc/g-atom. This value for gold is not far different from the value reported above, i.e., $\chi V_{\text{gold}} = 5.8$ cc/g-atom.

SUMMARY

A high-precision fast adiabatic microcalorimeter for studying energy released on annealing quenched-in imperfections in metals is described. Results obtained for gold are presented having an uncertainty of less than ± 0.002 cal/gram. Prior to this, quenched-in defects in metals have been studied primarily by the resistometric technique and recently supplemented with volume change studies.

The activation energy of formation of the defect determined from the calorimetric work is, $E_f = 0.97$ ev in good agreement with the value obtained from resistometric studies.

The activation energy of motion corresponds to those evaluated resistometrically and verify the temperature dependence of E_m on injection temperature, i.e., an increase in value with decrease in temperature of injection; $E_m = 0.73$ and 0.62 ev at $T_Q = 820^\circ\text{C}$ and 920°C , respectively.

Reaction rates of annealing of the defects appear to consist of first and second order components for the lower injection temperatures.

Since these calorimetric results seem to corroborate those obtained resistometrically, some of the data of both studies are combined to evaluate the following quantities based entirely on experimentally derived quantities and the assumption that the quenched-in defects are for the most part single vacancies: (a) Concentration of vacancies $C_v = \Delta E_T/E_f$, equals 1.5×10^{-4} at 920°C and 6.6×10^{-5} at 820°C . (b) Resistivity increase ($\mu\text{ohm-cm}$) per atomic percent vacancies, $(\Delta\rho_0/\Delta E_T/E_f) = 1.8 \pm 0.6$. (c) Increase in volume of the crystal per vacancy, $\chi = \Delta\rho/K'\Delta E_T/E_f = 0.57$.

The energy-resistance ratio, $\Delta E_T/\Delta\rho_0$, for quenched-in defects in gold has a value equal to 0.63 cal/gram $\mu\text{ohm-cm}$.

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