Slow quenches of high-quality single crystals of platinum and palladium

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(Received 31 July 1987)

A new technique for growing and quenching high-purity, low-dislocation-density single crystals has been developed. This quenching technique traps at least 87% of the vacancy concentration at 90% of the melting point without significantly increasing the dislocation density during the quench. Vacancy formation energies and entropies can then be determined more reliably. It also provides high-quality single crystals with a controllable supersaturation of vacancies for study by other techniques such as the de Haas–van Alphen technique. These studies can be made without significant background signal from impurities or dislocations. The technique has been tested on platinum and palladium.

I. INTRODUCTION

Numerous techniques have been developed to determine the thermal equilibrium properties of lattice vacancies in metals. Quenching to trap the high-temperature defect population for investigation at low temperature is a widely used method. The concentration of vacancies and their energy of formation can be determined from the temperature dependence of the resistance quenched in. As in all nonequilibrium techniques, results can be biased by defect losses during the quench. The loss rate depends primarily on the ratio of the defect mobility to the sink density. Since mobility increases with temperature, the fractional defect loss also increases and yields, for example, formation energy values which are too low.

Historically, the approach to reducing losses was to reduce the cooling time, i.e., to increase the quench rate. Small diameter (0.08–0.4 mm) polycrystalline samples thrust into chilled brines have yielded the highest rates. Negligible vacancy losses during quenches from 950 °C have been reported by Lengeler[1] for gold and by Bourrassa and Lengeler[2] for copper. They quenched 1.0-mm-diam single-crystal samples having dislocation densities, determined before quenching by etch pit counting, of $2000/cm^2$, into a -70 °C water–hydrochloric-acid bath. However, their de Haas–van Alphen investigation of the scattering of the conduction electrons by vacancies was marred by the strong background scattering at dislocations produced by the quench.[3] Indeed, the rapid quenches raised the dislocation density several orders of magnitude.[3,4]

Emrick[5] calculated vacancy losses during quench of low-dislocation-density crystals at a variety of quenching rates. These calculations showed that for dislocation densities even 2 orders of magnitude greater than those in Lengeler's samples,[1,3] vacancy losses of only a few percent would occur for cooling rates of hundreds of degrees per second rather than the 10^4 °C/sec of the water quenches.

The present work has been undertaken to develop a quenching technique that eliminates both the vacancy loss and the introduction of dislocations usually encountered during quench. This has permitted us to determine a more accurate value of the energy of formation of vacancies and to verify the prediction of the model proposed by Emrick.[5,6] The slow-quenched sample could also be used for other studies of vacancies, such as electron scattering. By aging such samples, the vacancy concentration could be changed without altering the low impurity and dislocation concentrations. In some metals, such as gold, vacancy clustering can be enhanced so that a wide range of vacancy concentrations and associations could be studied in the same single crystal.

Platinum was chosen for this study for several reasons. It can be purified by zone refining in air. It does not oxidize or absorb gases appreciably. Vacancy clustering is relatively unimportant[7] and the quenched state is stable at room temperature. Platinum has a relatively large equilibrium vacancy concentration at the melting point, so measurable concentrations can be observed over a wide range of quench temperatures. In addition, there is a vast store of data for making comparisons. Unfortunately we were unable to find a suitable etching technique, so that independent measurements of the dislocation density could not be made.

Palladium, on the other hand, has not been studied much by quenching, but can be handled as easily as platinum. Its formation energy has been measured by the positron annihilation method.[8] Indications were, however, that the vacancy concentration would be low.

II. EXPERIMENTAL METHOD

A. Sample preparation

The starting material for platinum samples was hard drawn 99.999% nominal purity 1-mm-diam wire obtained from Sigmund Cohn, Inc. Spectroscopic analysis showed detectable metallic impurities of 3 ppm Cu, 2 ppm Pd, and 1 ppm Rh. The potential leads were 0.08-mm reference grade Sigmund Cohn, Inc. platinum wires.

For palladium, the starting material was obtained from Johnson Matthey and Co., London, as 1-mm-diam wire of 99.999% nominal purity. Spectroscopic analysis

showed metallic impurities of 4 ppm Fe, 2 ppm Si, 1 ppm Ca, 1 ppm Cu, 1 ppm Ag, and 1 ppm Mg. The potential leads were cut from a 1-mm rod of palladium that had been rolled into a 0.08-mm-thick sheet.

The samples were further zone refined in air.[9] The residual resistivity ratio (RRR) corrected for finite size and extrapolated to absolute zero was in the range 7000–14 000 for platinum and 4800–27 000 for palladium.

B. Quenching techniques

Single-crystal samples were grown in the rf furnace by the floating-zone method from the purified wires. The potential leads, when used, were grown into the sample 2–3 cm apart.

1. Platinum

Two different methods of quenching were used. In the first, a single crystal was grown in a longer wire. At the end of the crystal the wire was melted through and a small support wire melted to the end. The wire was removed from the furnace and the other end of the crystal spark cut so that the 3-cm-long single crystal could be supported by the small wire from the quenching frame in the Metal Research PCA 10 furnace, as shown in Fig. 1. The sample was raised to the zero-gradient region and allowed to equilibrate at the quench temperature T_Q (up to 1400 °C) for an hour. Sample temperature was measured by either a Chromel-Alumel or a platinum 30% rhodium-platinum 6% rhodium thermocouple less than 1 cm away. New junctions were made every few runs and the calibration of the thermocouples checked against the melting point of reference-grade metal wires.[10] The sample frame then was released. It was stopped by a snubber so that the sample was in a stream of air from a cooling fan. Within 10–15 sec, the sample was placed in cold water for storage. Four terminal resistance measurements were made on the dried sample both at room and liquid-helium temperatures. The sample was then annealed for at least 4 h at 1100 °C, cooled at 100 °C/h to 400 °C where it was held for 12 h, and then cooled at 100 °C/h to room temperature. The RRR was again measured. The quenched-in vacancy resistance was taken to be the difference between the helium temperature resistance values.

In a variation of this method, the samples were hung from 0.08-mm-diam gold wires in the gradient-free region. The temperature was raised to about 1040 °C and equilibrated for an hour. It was then raised very slowly (about 1 °C/min) until the gold melted, allowing the sample to fall into a tank of chilled water. Then T_Q was taken to be 1063 °C.

In the second method, the sample was quenched in place in the rf furnace, minimizing contamination and dislocations produced by handling. This also permitted the use of a freshly grown sample for each quench. A detailed description of the apparatus is given by Khellaf.[10] Potential leads were grown into the sample 2 and 3 cm apart and a 15-A current was maintained while the single crystal was being grown. This dc current helped stabilize the molten zone and generate a voltage for temperature measurement. The molten zone was then moved to 5 cm below the gauge region, the dc current adjusted to achieve the desired temperature, and the rf power then quickly increased to melt through the wire.

Interruption of the dc current turned off the rf power and released a baffle allowing an air stream to flow over the sample. The brief increase in rf power caused no measurable sample temperature increase. The Johnson Mathey platinum resistance versus temperature scale was used. For $R(T)=R_0(1+AT^2+BT^3)$, $A=0.003\,977\,94\,°C^{-1}$, $B=-5.875\times10^{-7}\,°C^{-2}$, and R_0 is the 0 °C resistance. The sample annealing and the quenched-in vacancy resistance measurement procedures were the same as in the first method. Finally, at the end of each run the quality and the orientation of the sample were determined from a back-reflection Laue pattern.

2. Palladium

All the palladium quenches were carried out in the rf furnace. The same setup and procedure used to quench platinum in the rf furnace were used here. A suitable resistance temperature scale was not available, so $R(T)$

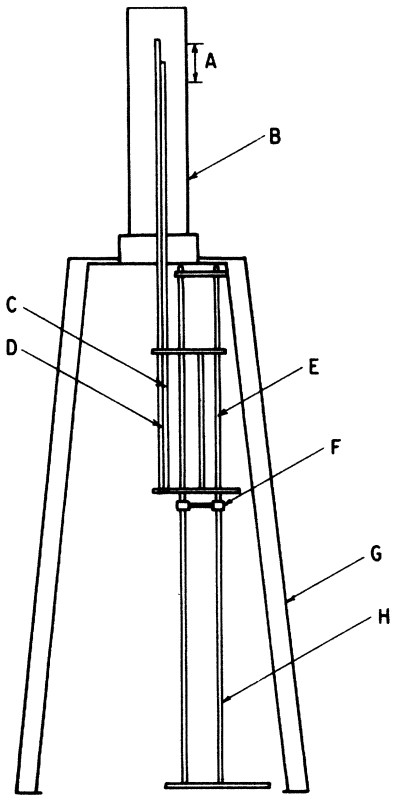

FIG. 1. Quenching apparatus in Metal Research (MR) furnace. *A*, uniform temperature zone; *B*, MR furnace; *C*, four-hole, $\frac{1}{4}$ inch high grade alumina (sample holder); *D*, four-hole, $\frac{1}{4}$ inch high grade alumina (thermocouple holder); *E*, moving sample holder (in fully up position); *F*, detent; *G*, furnace stand; *H*, sample holder frame. The rods are not parallel so that falling holder stops slowly.

was determined up to 1400 °C. The results have been reported elsewhere.[11]

III. RESULTS AND DISCUSSION

A. Platinum

Figure 2 presents our results for platinum. The solid line is a linear regression fit of the data. One of the major problems we encountered during quenching was the loss of vacancies due to the striation of the samples. The quenched-in vacancy concentration was as much as 50% smaller for striated samples than for striation-free samples. Data were rejected if x-ray analysis of the quenched sample showed striation or a twinning pattern.

The linear fitting of $\Delta R(T)/R_{20} = A \exp(-E_f/kT)$ to the data gives

$$A = 39 \pm 6$$

and

$$E_f = 1.24 \pm 0.07 \text{ eV} .$$

$\Delta R(T)$ being the resistance quenched in from T, R_{20} the resistance of the sample at 20 °C, k the Boltzmann constant, A the entropy factor, and E_f the energy of formation of vacancies.

However, a least-squares fit of the same relation to the data for T_Q below 1200 °C gives

$$A = 66 \pm 17$$

and

$$E_f = 1.30 \pm 0.03 \text{ eV} .$$

The energy of formation is roughly 5% higher than the one derived from the fit of the whole set of data. The most likely explanation is that there have been small vacancy losses for T_Q above 1200 °C. Extrapolating the low T_Q results to higher temperatures, we have found losses of 13% at 1500 °C and 10% at 1400 °C. The quenching rates have not been measured. However, quenching rates under similar circumstances have been determined, by direct measurements on 1-mm-diam gold rods, to be 160 °C/sec to 300 °C/sec.[12]

The dislocation density of our samples can be estimated using the model calculation proposed by Emrick.[5,6] This theoretical model considers only single vacancies migrating to fixed sinks. Clustering, variable sink efficiencies, and impurity binding are perturbing parameters that can influence the results. For example, divacancies migrate more rapidly than single vacancies, so they would lead to a greater loss than predicted by the model.

This model, reasonably accurate at dislocation densities up to $10^8/\text{cm}^2$, is a random array of parallel dislocation lines which maintain the instantaneous equilibrium vacancy concentration during quench. Figure 3 shows the fraction of the vacancy concentration retained at different T_Q as a function of the dislocation density for quenching rates from 160 °C/sec to 300 °C/sec. The re-

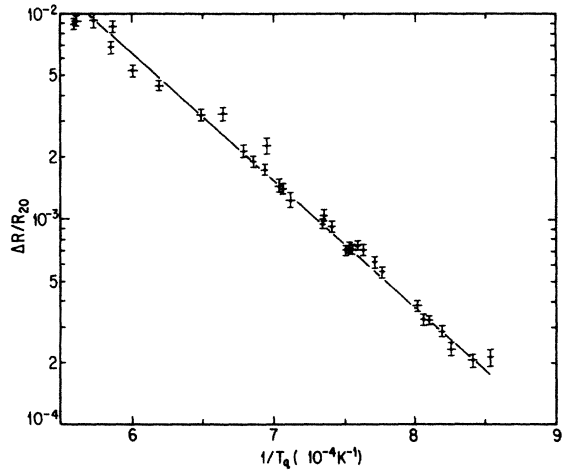

FIG. 2. Results for platinum single-crystal samples. Quenched-in resistance, normalized to the resistance of the sample at 20 °C, as function of the reciprocal absolute quench temperature.

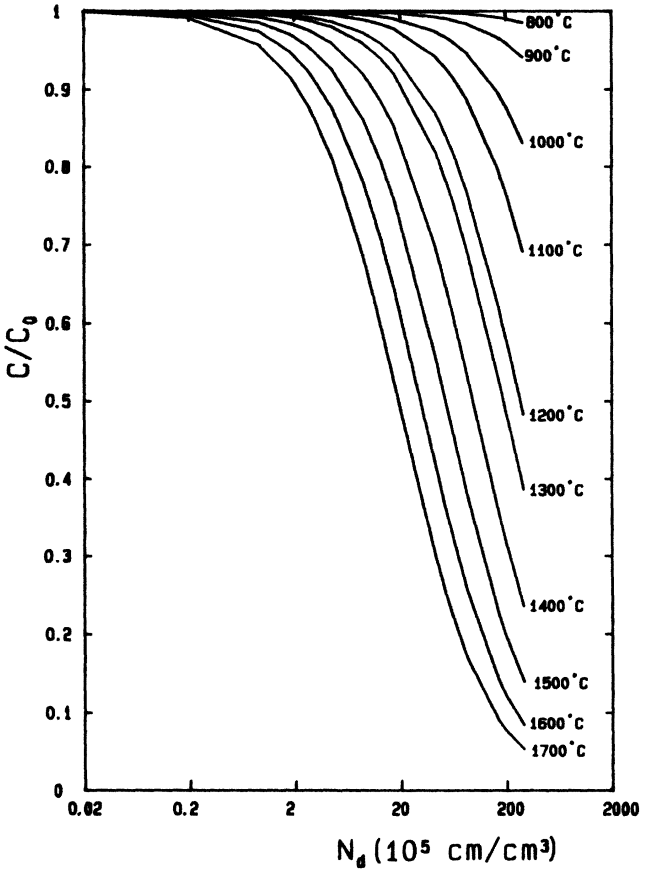

FIG. 3. Remaining vacancy concentration as function of the dislocation density for quench temperatures between 800 °C and 1500 °C. The quenching rate is 160 °C/sec–300 °C/sec. The model is single vacancies migrating to a random array of parallel dislocation lines which maintain the instantaneous thermal equilibrium vacancy concentration. $E_m = 1.38$ eV and $\nu = 1 \times 10^{13}$ sec^{-1} (similar results were obtained using $E_m = 1.60$ eV and $\nu = 2 \times 10^{13}$ sec^{-1}).

sults imply a dislocation density in the present samples in the range $5\times10^5/cm^2-10^6/cm^2$. This is in agreement with the preliminary measurements of low angle electron scattering by the de Haas–van Alphen (dHvA) technique using scattering parameters based on copper crystals with known dislocation density.[13,14]

The present value of the energy of formation of vacancies of 1.30±0.03 eV is in good agreement with the values determined by quenching by Misek[15] and by positron annihilation by Maier *et al.*[8] Zetts and Bass[16] found a similar value by applying by Flynn-Bass-Lazarus[17] theory to their quench results. However, the present value is larger than the 1.15-eV value reported by Emrick[12] and much lower than the 1.50-eV value reported by Jackson.[4] Even though the starting samples Emrick used are similar to the ones used in this study, his technique strained the samples during handling before the quench, thus increasing the dislocation density and the vacancy losses. Jackson used small-diameter high-purity polycrystal samples and carried out a careful analysis of the data. However, his measurements were made over the small, low-temperature range 650–900 °C. It has been argued[12,15,16] that the large value determined by Jackson and believed until a few years ago to be the "best value" is due to his assignment of more weight to the low-temperature data than can be justified.

Using the results of the data fitted up to 1200 °C, we have the entropy factor $A=66\pm17$. The resistivity per unit concentration of vacancies has been reported to be 4.6×10^{-4} Ω cm/at.-fraction.[18] Combining these data and taking the platinum resistivity at room temperature to be 10.63 μΩ cm (converted from the $\rho_{0°C}=9.876$ μΩ cm of Flynn and O'Hagan[19]), the entropy of formation is found to be $(0.42\pm0.11)k$. This value is at the low energy of the range found for most fcc metals, $0.7-2.4k$ as reported by Siegel.[20]

In addition, with $E_f=1.30$ eV and the above values, the concentration of vacancies at the melting point, $T_m=1769$ °C, can be calculated from the equation $C_v=\exp[(TS_f-E_f)/kT]$ to be $C_v=(9.4\pm0.7)\times10^{-4}$. As reported in Table I, this result is in good agreement with the quenching values reported by Schumacher *et al.*[21] and by Zetts and Bass[16] and the positron annihilation value reported by Schaeffer.[18] However, it is much smaller than the dilatometry value reported by Kraftmakher and Strelkov[22] and the quenching value reported by Zetts and Bass[16] derived from Jackson's data.[4] The low values are more likely to be correct due to the better control of the experimental parameters that affect the results. Since the measurements in the dilatometry method involve small differences in large quantities, the uncertainty in the determination of the vacancy concentration is very large. The same argument can be used for the specific-heat measurements. The large value derived from Jackson's data could be due to the extrapolation of the data from 900 °C to the melting point.

The present results are compared to previous air-quench results of some other workers in Fig. 4 and to earlier fast-quench results in Fig. 5. These figures show that, even though the present cooling rates are much smaller, the linearity of the Arrhenius plot extends over a larger temperature interval. This proves that fast quenches are not necessary to trap essentially all the equilibrium vacancy concentration in low-dislocation-density samples, as predicted by Emrick.[5,6]

To show the effect of the dislocation density on the fraction of the equilibrium vacancy concentration quenched in a sample, we compare our results to those of Zetts and Bass[16] in Fig. 6. Their polycrystal-sample results have been chosen for comparison because the samples have a purity, as measured by RRR, comparable to the present samples. Since the purity is the same, the difference in the results should then be attributed to the

TABLE I. Platinum vacancy concentration at the melting point.

$10^4\ C_v(T_m)$	Method	Reference
24	Quenching	3
26	Dilatometry	27
100	Specific heat	22
8.4	Quenching	21
10	Quenching	16
10.2	Positron	18
9.4	Quenching	Present work

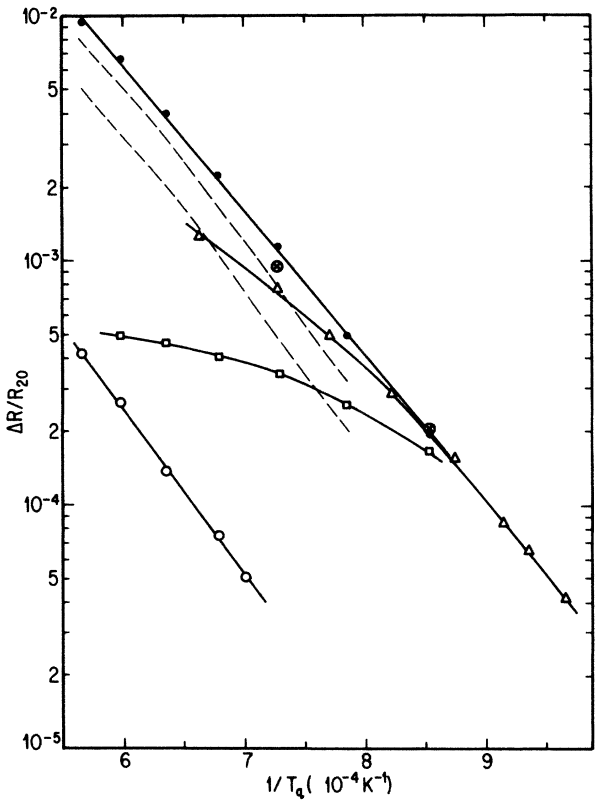

FIG. 4. Comparison with previous slow-quench results. Normalized resistance air-quenched into platinum as function of the inverse absolute quench temperature. ●, present work; ○, Ascoli *et al.* (Ref. 23); ⊗, Misek (Ref. 15); △, Zetts and Bass (Ref. 16); — — —, Bradshaw and Pearson (Ref. 24) 95% probability zone.

dislocation density. The actual dislocation density of Zetts and Bass's polycrystal samples has not been reported. Using the model calculation proposed by Emrick[5] and their air-quench results, the dislocation density was found to be in the range $(0.9-1.5)\times10^8/cm^2$. In contrast, the present single-crystal samples have a dislocation density of no more than $10^6/cm^2$. Using the same model calculation, Zetts and Bass's linear water quenches have, however, yielded a slightly larger value, $(2.5-4)\times10^8/cm^2$. This is to be expected since water quenching would lead to the straining of the samples.[4]

B. Palladium

The resistance quenched in the high-quality crystals was very small. Its uncertainty was at least 10% for the highest T_Q. Thus, scatter at lower T_Q prevented a determination of even E_f. As would be expected, the increase in resistance was much larger for impure samples. Orienting the sample growth axis along [110] and [100] did not alter the results.

To our knowledge, there are no other quench data for palladium. In positron annihilation studies, E_f and C_v have been determined to be, respectively, 1.85 ± 0.25 eV by Maier *et al.*[8] and 0.14×10^{-4} by Schaeffer.[18] Using our highest T_Q values, we have found the palladium specific vacancy resistivity to be $(1.6-4.0)\times10^{-4}$ Ω cm(at.-fraction)$^{-1}$. This is the same magnitude as reported for gold[1] and platinum.[18] The present low quenched-in resistance values found in palladium are then due to the large value, compared to that of gold and platinum, of its energy of formation.

IV. CONCLUSIONS

A technique to produce and quench large-diameter, high-purity, low-dislocation-density metal crystals has been developed. This technique is an improvement over previous ones in that it eliminates the introduction of unwanted dislocations during quench. A new crystal is grown each time and is not handled until after the slow air quench is complete.

The technique has been applied to quench high-purity platinum single crystals. The results show that there has been a drastic reduction in the vacancy losses that usually occur at T_Q above 1000 °C. The energy of formation of vacancies has been found to be $E_f=(1.30\pm0.03)$ eV. The entropy of formation and the concentration of vacancies at the melting point have been estimated to be, respectively, $S_f=(0.42\pm0.11)k$ and $C_v(T_m)=(9.4\pm0.7)$

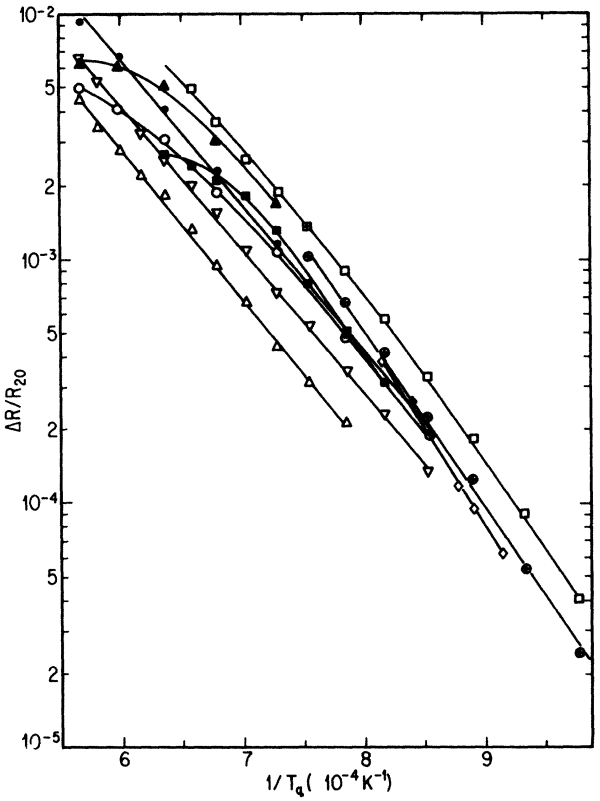

FIG. 5. Comparison with previous fast-quench results. Normalized resistance water-quenched into platinum as function of the inverse absolute quench temperature. ●, present work; ○, Zetts and Bass (Ref. 16); ◇, Heigel and Sizman (Ref. 25); ⊗, Charles *et al.* (Ref. 26); □, Jackson (Ref. 4); △, Ascoli *et al.* (Ref 23); ▽, Bacchella (Ref. 27); ◆, Kopan (Ref. 28); ▲, Rattke *et al.* (Ref. 29).

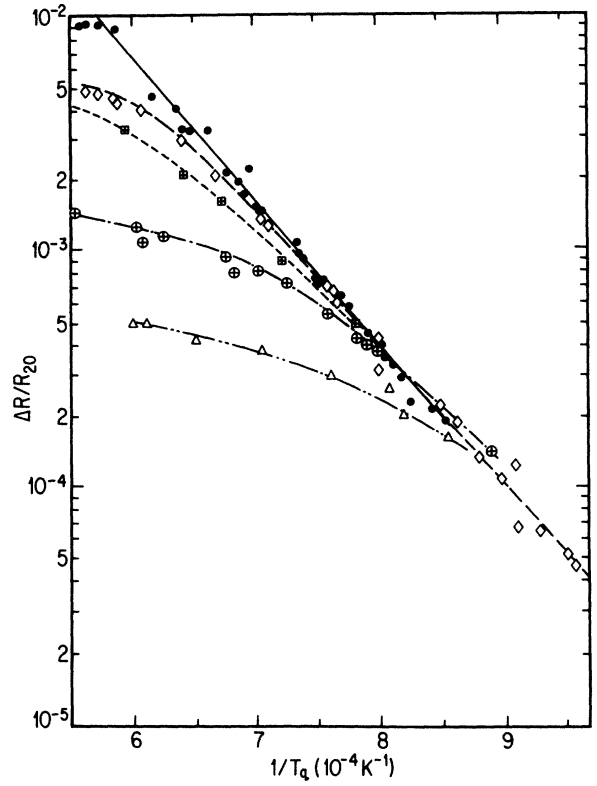

FIG. 6. Comparison with Zetts and Bass's results. Normalized resistance quenched into high-purity platinum, using different quenching rates, as function of the inverse absolute quench temperature. Zetts and Bass's results have been chosen because the samples used have a purity, as measured by the residual resistance ratio, comparable to the ones used in the present work. ●, present work; ◇, water quench, ⊞, kerosene quench; ⊗, helium gas quench; △, air quench.

$\times 10^{-4}$. The data have been analyzed using a sink model for vacancy loss proposed by Emrick.[5,6] It is a cylindrical model where the core has been assumed to drain the cylindrical volume. It was found that the present results are in good agreement with the model predictions.

High-purity palladium single crystals have also been quenched using the same method. Although an increase in resistance has been observed, it has been impossible to determine any thermodynamic variable associated with vacancies in palladium because of the large scattering of data.

We believe that the present quenched samples are ideal for detailed studies of the scattering of conduction electrons by vacancies using the dHvA technique. Only vacancies and divacancies distributed randomly are quenched in. Since the samples are of high purity and nearly dislocation-free, the effect of point defects can be studied separately.

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