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# The vacancy formation energy in platinum

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ABSTRACT

The resistivities quenched into Pt wires of diameters 16 mil, 10 mil, and 4 mil have been measured as a function of quench temperature for a variety of quench speeds, and the data have been analysed in terms of the Flynn, Bass, and Lazarus (FBL) theory of vacancy-annealing to fixed sinks during a quench. The data are consistent with all predictions of the theory. For fast quenches from below 950°C, where few if any vacancies should be lost during the quench, the data for the different wire diameters yield effective formation energies, $E_f^{eff}$, ranging from 1·16 to 1·35 eV. Application of the FBL theory to the whole of the data for the same samples yields values for $E_f$ ranging from 1·25 to 1·35 eV. Combining these results, taking into account the fact that $E_f^{eff} \leqslant E_f$, and allowing for known possible systematic errors, a 'best estimate' for $E_f$ in Pt is $1 \cdot 3 \pm 0 \cdot 05$ eV. This value is consistent with 1·35 eV, as recently suggested by Misek, but is nearly 15% lower than the generally accepted value of 1·5 eV, as first proposed by Jackson.



## § 1. INTRODUCTION

### 1.1. *The genesis of the present study*

For nearly two decades, attempts have been made to measure the formation energy $E_f$ and the motion energy $E_m$ of vacancies in pure metals. A variety of both thermal equilibrium and quenching studies have confirmed that the fractional vacancy concentration $c$ in thermal equilibrium at the absolute temperature $T$ can be described by the relation

$$c = \exp(S_f/k)\exp(-E_f/kT), \tag{1}$$

where $k$ is Boltzmann's constant and $S_f$ is the entropy-increase per vacancy. The vast majority of these studies have involved quenching to a low temperature where the vacancies are immobile, followed by measurements of quenched-in resistivity. These measurements have been used to infer values for $E_f$. Subsequent low-temperature annealing studies have been used to infer values for $E_m$. It has normally been assumed that the correct values of $E_m$ and $E_f$ should sum as

$$E_f + E_m = Q, \tag{2}$$

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where $Q$ is the activation energy for self-diffusion. Equation (2) should hold if self-diffusion takes place solely by means of single vacancies whose concentration is described by eqn. (1).

In this laboratory, studies have been made of how the resistivity quenched into wires of pure Au (Flynn, Bass and Lazarus 1965), Al (Bass 1967), and W (Gripshover, Khoshnevisan, Zetts and Bass 1970) varied with quench temperature and quenching speed, and the resulting data have been used to obtain values for $E_f$ and $E_m$. The advantage of these studies was that they used only data taken at high temperatures, where effects of vacancy–vacancy and vacancy–impurity interactions are minimal (Flynn, *et al.* 1965, Balluffi, Lie, Seidman and Siegel 1970). This contrasts, for example, with low-temperature annealing studies used to infer values for $E_m$, since annealing behaviour is known to be very sensitive to both vacancy–vacancy and vacancy–impurity interactions (Chik 1970, Seeger and Mehrer 1970, Burton and Lazarus 1970).

In the above studies the data were analysed using the FBL theory (Flynn *et al.* 1965) and assuming the validity of eqn. (2). The present study began when it was realized that published data strongly suggested that values for $E_f$ and $E_m$ could be obtained for Pt using the FBL theory alone, without requiring in advance that eqn. (2) be valid. Equation (2) could then be used to test the applicability of the theory to Pt, the theory being supported if eqn. (2) were found to hold.

The paper is organized as follows. First, the assumptions underlying the FBL theory are outlined and the method for determining values for $E_f$ and $E_m$ is described. Emphasis is placed both on the limitations of the theory and on the importance of the contemplated test of its applicability. Next, a review of published data is used to establish the suitability of Pt for the proposed test. The samples used in the experiment are then described, along with relevant experimental details. New data for fast quench speeds are then presented and shown to disagree with the generally accepted ' best values ' for Pt. The relative merits of the new and older data are examined. New data are then presented for a variety of quench speeds and are analysed in terms of the FBL theory. Finally, the significance of the new results is discussed.

### 1.2. *The FBL theory and its limitations*

If a sample could be cooled sufficiently rapidly to trap all the vacancies initially present at the quench temperature $T_q$, then from eqn. (1) the increment in resistance $\Delta R_q$, produced by the quench (the *quenched-in resistance*) would be given by

$$\Delta R_q = R_v \exp(S_f/k) \exp(-E_f/kT_q), \tag{3}$$

where $R_v$ is the resistance of a unit concentration of single vacancies. A plot of $\ln \Delta R_q$ versus $1/T_q$ would then yield a straight line, the slope of which would be $E_f/k$. In practice, even with the fastest attainable quench speeds, there is usually some vacancy-loss during the quench, the largest fractional losses occurring for the highest quench temperatures. In this case, the variation of $\Delta R_q$ with $T_q$ would not reproduce eqn. (3) exactly, and a plot of $\ln \Delta R_q$ versus $1/T_q$ would, in general, not yield a straight line. At best a lower limit for $E_f$ could be obtained, by fitting a straight line to the lower quench-temperature data where the fractional vacancy loss is smallest. The slope of such a line will be described in terms of an *effective formation energy*, $E_f^{eff}$, which should be less than or equal to $E_f$.

To determine $E_f$ it would be necessary to correct for vacancy-loss during the quench. In principle this could be done by measuring the increase of quenched-in resistivity with decreasing quench time, and then extrapolating to an infinitely rapid quench. Unfortunately, in the general case, this extrapolation requires a complete solution of the diffusion equation, taking into account the changing concentrations and mobilities of both single vacancies and small vacancy clusters, and the nature and concentrations of the sinks at which these vacancies and clusters are annihilated. But if this information were available, it would be unnecessary to make the extrapolation in the first place.

Even in the simplest possible case, where during the quench single vacancies migrate, without clustering, to fixed sinks, the diffusion equation cannot be solved exactly without knowledge of the nature and concentrations of these sinks. However, in this simple case, FBL discovered that it is possible to determine $E_f$ without detailed knowledge about the sinks, provided either that $E_m$ is known, or that eqn. (2) holds.

They showed that so long as the nature and number of sinks are the same for all quench temperatures and quenching speeds, the fractional concentration of vacancies retained during a quench will depend only upon the single variable $Z = D_q T_q \tau_q$. Here $D_q$ is the single-vacancy diffusion coefficient at the quench temperature $T_q$, $\tau_q$ is the quench-time defined through the time-dependent cooling curve

$$T(t) = \frac{T_q}{1 + \dfrac{t}{\tau_q}} \tag{4}$$

and $t$ is the time measured from the start of the quench. $D_q$ has the form

$$D_q = D_v \exp(-E_m/kT_q), \tag{5}$$

where $E_m$ is the single-vacancy motion energy.

To test the applicability of the FBL theory, it is first necessary to confirm that the fractional vacancy concentration retained during the quench is indeed a function only of $D_q T_q \tau_q$, as was found to be the case in previous studies. The FBL theory then determines a relationship between $E_f$ and $E_m$, such that given one of these quantities the experimental data determine the other. Unfortunately, in the earlier studies of Au, Al and W, it was not possible to determine either $E_f$ or $E_m$ independently, and eqn. (2) was used to determine both, so that the conclusions drawn rested upon two assumptions : (1) that eqn. (2) was valid for each of the metals studied ; and (2) that the observation that the quenched-in resistivity was a function only of the product $D_q T_q \tau_q$ could be taken as proof that the FBL theory was applicable to the data. Both assumptions have been questioned.

(1) Evidence of curvature in the Arrhenius plot for Au led Seeger and Mehrer (1968) to question the applicability of eqn. (2) to self-diffusion data for this metal, and to propose the values $E_f = 0{\cdot}87$ eV and $Q = 1{\cdot}76$ eV for

single vacancies, both considerably smaller than the FBL values $E_f = 0{\cdot}97$ eV and $Q = 1{\cdot}8$ eV. To rationalize the disagreement between the values for $E_f$, they suggested that the FBL analysis might have suffered from a systematic error associated with increasing quenching strain as the quench-speed increased. New evidence on this point is given below.

(2) Perry (1970) has argued that the quenched-in resistivity can be a function of $D_q T_q \tau_q$ even when vacancies cluster to form mobile divacancies during the quench. His argument is based upon a rate-equation analysis, which is only approximate. Nonetheless it does suggest the need for caution in concluding that the expected dependence is evidence for lack of vacancy-clustering.

In view of these arguments it was decided to reinvestigate the adequacy of the FBL theory under more stringent conditions ; a three-step test was envisaged : (1) Determine $E_f$ directly from low-temperature quenching under conditions where vacancy-loss during the quench should be negligible. (2) Measure the variation of quenched-in resistivity with quenching speed at higher temperatures ; test for the expected dependence on $D_q T_q \tau_q$ and, if this dependence is observed, determine $E_m$ using the $E_f$ determined in step No. 1. (3) Add $E_f$ to $E_m$ to see whether eqn. (2) is obeyed. If it is, this would constitute a more convincing verification of the FBL theory and a more definite determination of $E_f$ and $E_m$ than had hitherto been possible.

### 1.3. *The suitability of Pt for testing the FBL theory*

Except for gold and aluminium, Pt has been studied by quenching more than any other metal. In addition, there exist for Pt two independent self-diffusion studies (Kidson and Ross 1957, Cattaneo, Germagnoli and Grasso 1962), in good agreement with each other, which yield $Q \simeq 2{\cdot}9$ eV, with little or no evidence of curvature in the Arrhenius plot. The quenching studies are listed in table 1 along with the self-diffusion studies.

Between 1955 and 1961 there were six studies of quenched Pt, five of which yielded values for $E_f$. These values ranged from 1·2 to 1·4 eV. Associated annealing studies yielded values for $E_m$ varying from 1·1 to 1·5 eV. Although the sum of the maximum values obtained for $E_f$ and $E_m$ is approximately equal to the activation energy for self-diffusion, $Q = 2{\cdot}9$ eV, it is perhaps significant that no single investigator obtained values for $E_f$ and $E_m$ whose sum was so large. In 1964, however, Misek reported the values $E_f = 1{\cdot}24$ eV and $E_m = 1{\cdot}7$ eV, which summed to 2·94 eV. Subsequently Kopan (1965) reported the higher value $E_f = 1{\cdot}42$ eV, and Jackson (1965 a) reported the substantially different values $E_f = 1{\cdot}51$ eV and $E_m = 1{\cdot}38$ eV. Jackson proposed a consistent interpretation of nearly all the existing data based upon the propositions that the value 1·1 eV (usually obtained from anneals after quenches from high temperatures) corresponded to the motion energy for divacancies $E_m^{2v}$, and that the value $E_m = 1{\cdot}4$ eV (usually obtained from anneals after quenches from lower temperatures) corresponded to the motion energy for single vacancies. He argued that earlier investigators had obtained values for $E_f$ less than 1·5 eV because of systematic errors associated with their experimental conditions. In particular, he argued that they had used wires which were too thin and of insufficient purity, and quenched from

Table 1. Previous studies of vacancies in platinum.

A. Quenching and annealing experiments using electrical resistance measurements

| | $E_f$ (eV) | $E_m$ (eV) | $E_f+E_m$ (eV) | Investigators |
|---|---|---|---|---|
| (1) | 1·2 | 1·1 | 2·3 | Lazarev and Ovcharenko (1955) |
| (2) | 1·4 ± 0·1 | 1·2 ± 0·1 | 2·6 | Bradshaw and Pearson (1956) |
| (3) | 1·23 | 1·42 | 2·65 | Ascoli *et al.* (1958) |
| (4) | 1·2 ± 0·04 | 1·48 ± 0·08 | 2·68 | Bacchella *et al.* (1959) |
| (5) | | 1·13 | | Piercy (1960) |
| (6) | 1·24 | 1·7 | 2·94 | Misek (1964) |
| (7) | 1·42 | | | Kopan (1965) |
| (8) | 1·51 ± 0·04 | 1·38 ± 0·05 | 2·89 | Jackson (1965 a) |
| (9) | | 1·50 | | Polak (1968) |
| (10) | | 1·33 ± 0·05 | | Schumacher *et al.* (1968) |
| (11) | | 1·35 ± 0·05 | | Rattke, Hauser and Wieting (1969) |
| (12) | 1·51 ± 0·02 | | | Heigl and Sizmann (1972) |
| (13) | 1·35 | | | Misek (1974) |
| (14) | 1·3 ± 0·05 | | | Present work |

B. Other methods

| $E_f$ (eV) | Property measured | Investigators |
|---|---|---|
| 1·4 | Thermoelectric force | Gerstriken and Novikov (1961) |
| 1·6 | High-temperature electrical resistance and specific heat | Kraftmakher and Lanina (1965) |

C. Self-diffusion experiments

| $Q$ (eV) | Investigators |
|---|---|
| 2·96 ± 0·06 | Kidson and Ross (1957) |
| 2·89 ± 0·04 | Cattaneo *et al.* (1962) |

too high temperatures. Jackson also interpreted his data in terms of a divacancy binding energy $E_b^{2v}$ of 0·4 eV, approximately 25% of $E_f$. Over the next few years, Jackson's values came to be generally accepted for Pt, with the exception of his large value for $E_b^{2v}$. Schumacher, Seeger and Harlin (1968) proposed the alternative value $E_b^{2v}=0·1$ eV, and subsequent work has tended to support a considerably smaller value such as this. The most important single piece of evidence is the recent Field Ion Microscope study by Berger, Seidman and Balluffi (1973), who found only 6% divacancies among the vacancies observed after quenches from very near the melting-point.

When the present study began, it thus appeared: (1) that $E_f$ could be determined directly from low-temperature quenching measurements, and that its value lay in the vicinity of 1·5 eV; (2) that $E_m$ could be determined directly from annealing studies after medium-temperature quenches, and that its value lay in the vicinity of 1·4 eV; (3) that there was little if any curvature in the Arrhenius plot for self-diffusion in Pt, and that $Q \approx 2{\cdot}9$ eV; (4) that $E_f$ and $E_m$ summed to give this $Q$; (5) that vacancy–vacancy binding in Pt was probably small enough to allow neglect of divacancy formation when applying the FBL analysis to quenching data. While the present study was in progress, Heigl and Sizmann (1972) reported additional support for a value of $E_f$ in the vicinity of 1·5 eV. For all these reasons, Pt seemed ideal for testing the FBL model.

In view of the emphasis placed by both Jackson and Schumacher *et al.* on the importance of quenching strains, it was decided to quench wires of three different diameters—16 mil (0·4 mm), 10 mil (0·25 mm), and 4 mil (0·1 mm)—reasoning that the wires of different diameters would experience different quenching strains. In addition, for the thicker wires two different quenching systems were assembled for the control and variation of the fastest liquid-quench speeds in different ways. Moreover, the thicker wires were quenched in both liquids and gas; the thinnest wires only in gas. Finally, several wires of each diameter, subjected to a variety of annealing treatments, were quenched in order to ascertain whether different annealing treatments led to different data. The results of the measurements are described below, after a brief discussion of sample preparation and experimental details. A more detailed examination of these subjects is given by Zetts (1971), who also discusses the accuracy of the experimental data.



## § 2. Specimen preparation and experimental information

### 2.1. *The specimens*

All samples used in this investigation were reference grade (99·999% pure) Pt, obtained as hard-drawn wire from the Sigmund Cohn Corporation. The potential leads, which were spot-welded to the samples, were also reference grade Pt. For sample diameters of 16 mil, 10 mil and 4 mil, the potential leads were respectively chosen to be 2 mil, 2 or 0·6 mil, and 0·6 mil in diameter. The overall length of the specimens varied from 3 to 5 in., and the gauge length, determined by the separation between the potential leads, varied from 1 to 2 in. The potential leads were placed as far apart as possible, consistent with good temperature uniformity along the gauge length. Prior to quenching, all samples were examined for temperature uniformity along the gauge length. Since the samples were visibly glowing at all but the very lowest quench temperatures, any substantial temperature variations could easily be detected, and samples manifesting any variation were discarded.

### 2.2. *Annealing procedure*

After mounting on a holder, the specimens were resistance-heated in air and given an initial anneal to promote grain growth and to minimize dislocation density. For the 16 mil specimens this originally consisted of ½ to

1 hr at 1600°C, 10 hrs at 1400°C, and 10 hrs at 800°C, followed by half-hour steps of 100° each down to 500°C, after which the current was turned off. This anneal produced a residual resistance ratio RRR ($\mathrm{RRR} = R_{239\mathrm{K}}/R_{4\cdot2\mathrm{K}}$) of 5000 or greater, comparable to the values obtained by Jackson (1965 a). It was later found that the high-temperature annealing times could be reduced by more than half with little change in RRR, and so later samples were given shorter anneals. A similar annealing procedure was initially used for the 10 mil specimens and produced RRR's of about 9000. However, as the long anneal at high temperature produced substantial stretching and thinning of the specimens, a shorter anneal was later adopted. It consisted of a few minutes of 1400°C and a few hours at 900°C, followed by slow cooling. This produced RRR's in the vicinity of 4000 and very similar quenched-in resistivities to those obtained after the longer anneals.

Table 2. Annealing procedures and residual resistance ratios (RRR).

| Specimen number | Type of anneal | RRR | Letter code |
|---|---|---|---|
| 16 mil specimens | | | |
| 1 | a | 5470 | *a*—long, high-temperature anneal (10 hours or more at 1400°C or higher) |
| 3 | a | 5600 | |
| 6 | a | 5500 | |
| 7 | a | 1130 | b—intermediate-temperature anneal (less than 5 hours at 1400°C or higher) |
| 8 | b | 5270 | |
| 9 | b | 4000 | |
| 10† | b | 4920 | |
| 11 | b | 5702 | |
| 12 | a | 4940 | *c*—low-temperature anneal (never annealed above 1250°C) |
| 10 mil specimens | | | d—short, high-temperature anneal (5 min or more at 1300°C or higher) |
| 4 | a | 9980 | |
| 5 | a | 8990 | |
| 6 | b | 5550 | |
| 7 | b | 3920 | f—isochronal anneal (100–1000°C) |
| 8 | b | 3170 | |
| 9 | b | 4490 | |
| 4 mil specimens | | | |
| 1 | c | 3960 | |
| 4 | d | 214 | |
| 5 | d | 318 | |
| 6 | f | 2820 | |
| 7 | c | 3090 | |
| 8 | c | 2550 | |
| 9 | c | 3090 | |
| 10 | c | 3300 | |
| 11 | c | 3180 | |

† Sample 10 was kindly supplied by Dr. J. J. Jackson. It was taken from the same roll as other specimens used in his study.

An even more restricted annealing procedure had to be used for the 4 mil (0·004 in.) wires. It was discovered that annealing at temperatures higher than about 1250°C for more than a few minutes produced quite low RRR's—in the vicinity of 250. However, anneals consisting of a few minutes at 1200 to 1000°C, and then a few hours at 800°C, produced RRR's greater than 3000, and this procedure was adopted.

The annealing history and RRR's of the samples investigated are given in table 2.

In addition to these initial anneals, all specimens were periodically given a cleansing anneal to produce a vacancy-free state. The resistance in this state is called the 'vacancy-free base resistance'. For the larger wires this anneal usually consisted of about 1 hr at 800°C followed by slow cooling. For 4 mil wires the anneal consisted of about $\frac{1}{2}$ hr at 800°C, followed by slow cooling. Longer anneals at temperatures above 1000°C were sometimes necessary for 16 to 10 mil specimens which had been liquid-quenched from high temperatures. Especially in the latter case, it was not always possible to reproduce exactly the pre-quench vacancy-free base resistance, which usually showed a small increase.



### 2.3. *Measurements of* $T_q$ *and* $\Delta R_q$

After each cleansing anneal, the resistance of the sample was measured at room temperature, and its value corrected to 20°C using the temperature coefficient of resistance $\alpha = 3{\cdot}9 \times 10^{-3}/°C$. This resistance was used both to determine the quench temperatures and to normalize the annealed and quenched-in resistances. The quench temperatures, $T_q$, were determined from the ratio $R(T_q)/R_{293K}$, using the N.B.S. values for the resistance of Pt as a function of temperature (Roeser and Wensel 1941). The quenched-in resistivities, $\Delta R_q$, are presented in the normalized form $\Delta R_q/R_{293\,K}$, so as to correct for differences in sample diameters and lengths.

### 2.4. *The two quenching systems*

For liquid quenches the 16 and 10 mil diameter wires were mounted in one of two different holders associated with two different quenching systems. Quench system No. 1 (QS No. 1) was similar to that originally developed by Bauerle and Koehler (1957). In this system the holder moved in an arc into the liquid, with the sample horizontal just at the liquid surface. Quench system No. 2 (QS No. 2) was similar to that used by Jackson (1965 a) in his study of Pt. In this system the sample was propelled by a spring vertically downward into the liquid. QS No. 2 allowed us to vary conveniently both the speed of entering the liquid and the final depth of immersion. When the sample was propelled rapidly deep into the liquid this system provided faster quenches than QS No. 1. Drawings of the two holders and more detailed descriptions of their use are given by Zetts (1971).

### 2.5. *Varying the quenching speed*

For the 16 mil wires different quench speeds were obtained by quenching the samples in water, kerosene, helium gas, and air. The fastest and slowest quench speeds differed by a factor of about 30.

For the 10 mil wires different quench speeds were obtained by quenching the sample in water and air, and also by reducing the heating current in a programmed manner while the sample was in air. Here the fastest and slowest quench speeds differed by a factor of nearly 200.

For the 4 mil wires different quench speeds were obtained by quenching the sample in air and also by reducing the heating current in a programmed manner while the sample was in air. The fastest and slowest quench speeds differed by a factor of about 60.

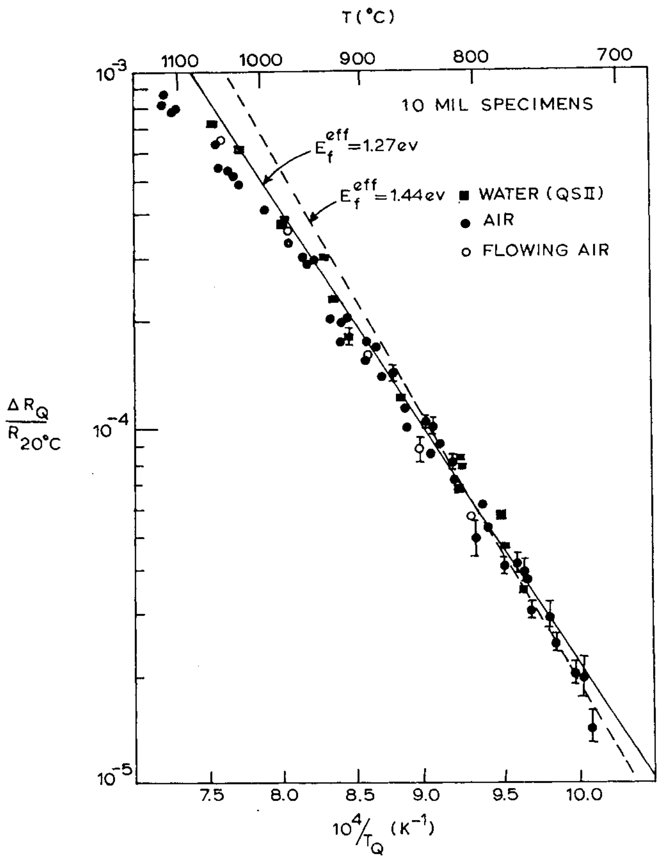
Typical quench curves and more detailed information about quench times are given in Zetts (1971).

## § 3. Experimental data and analysis

### 3.1. *Fast quenches from below 950°C : data*

As indicated above, an attempt was first made to reproduce Jackson's data for $T \leqslant 950°C$, where his results suggested that essentially all of the initial thermal equilibrium vacancy concentration should be retained during the fastest quenches achieved.

Fig. 1

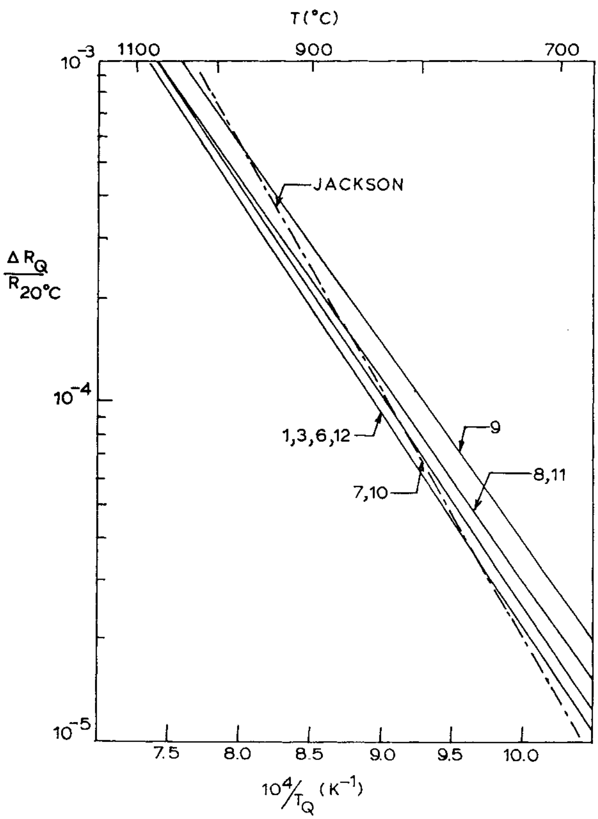



Resistance quenched into 10 mil wires for water quenches using QS 2. Air and flowing air quenches with the same specimens are included for comparison.

Figure 1 shows water-quench data for three 10 mil diameter wires quenched using QS No. 2. Data for still air and flowing air quenches are also included, since water and air quenches produced comparable quenched-in resistances for quench temperatures lower than 900°C and there is less scatter in the low-temperature air-quench data. Fitting the data up to 950°C yields $E_f^{eff} = 1 \cdot 27 \pm 0 \cdot 05$ eV. Additional measurements with other 10 mil samples yielded values of $E_f^{eff}$ ranging from 1·22 to 1·30 eV.

For 16 mil diameter wires quenched into water the values for $E_f^{eff}$ ranged from 1·16 to 1·23 eV when the data were fitted up to 950°C. Figure 2 shows best-fit straight lines to the data for all nine of the wires studied. For comparison, a best fit to a typical set of Jackson's raw data is indicated by the broken line. The slope of this line yields $E_f^{eff} \simeq 1 \cdot 43$ eV.

Fig. 2




Collected data for nine 16 mil specimens quenched into water. The specimens are numbered as in Table 1. Specimen No. 10 was kindly supplied by Dr. J. J. Jackson from the same roll as the other specimens which we measured. For comparison the broken line represents the data which Jackson obtained.

To minimize quenching strain, the 4 mil diameter wires were not quenched in water. Air quenches yielded values of $E_f^{eff}$ ranging from 1·20 to 1·35 eV when the data were fitted up to 950°C.

On comparing the values of $E_f^{\text{eff}}$ for the wires of three different diameters, it is seen that those for the 16 mil diameter wires are systematically lower than those for the 10 mil and 4 mil diameter wires—on the average by about 0·07 eV. This difference may arise, at least in part, from a small resistivity increment due to unavoidable strains produced by water quenches†. Jackson (private communication) found water quenches from the vicinity of 400–500°C to yield quenched-in resistivities of the order of $5 \times 10^{-11}\ \Omega$ cm, and subtracted such values from his data points to determine the resistivities due to quenched-in vacancies. Some quenched-in increments were observed after such low-temperature quenches in the present experiments, but these were small, their variation was comparable to their magnitude, and their magnitude was comparable to the variation in the vacancy-free base resistance. Thus no sufficiently reliable determination of their magnitude for general use was possible. Moreover, the temperature dependence of any strain-induced resistivity increment is unknown. For both reasons, no correction has been applied for any such increments. Where appropriate, the changes which such corrections would produce are discussed.



### 3.2. *Fast quenches from below 950°C: analysis*

From the numbers given above, if a fit up to 950°C is required, the data for all three wire diameters yield values of $E_f^{\text{eff}}$ less than 1·35 eV. This upper limit is 5% lower than the value for Jackson's sample (fig. 2), and 10% lower than his proposed value of $E_f = 1{\cdot}5$ eV. It was, of course, sometimes possible to obtain values of $E_f^{\text{eff}}$ greater than 1·4 eV by restricting the fit to still lower temperatures (see e.g. dashed line in fig. 1). However, with a more restricted temperature range, the inferred value for $E_f^{\text{eff}}$ is extremely sensitive to small variations in the magnitude of the data at the two ends of this range. Thus, modest uncertainties in the data, due both to variations in the vacancy-free base resistance and to limitations on measuring sensitivity (see, e.g. error bars in fig. 1), lead to large uncertainties in $E_f^{\text{eff}}$. This is the fundamental problem in attempting to determine $E_f$ directly from low-temperature quench data.

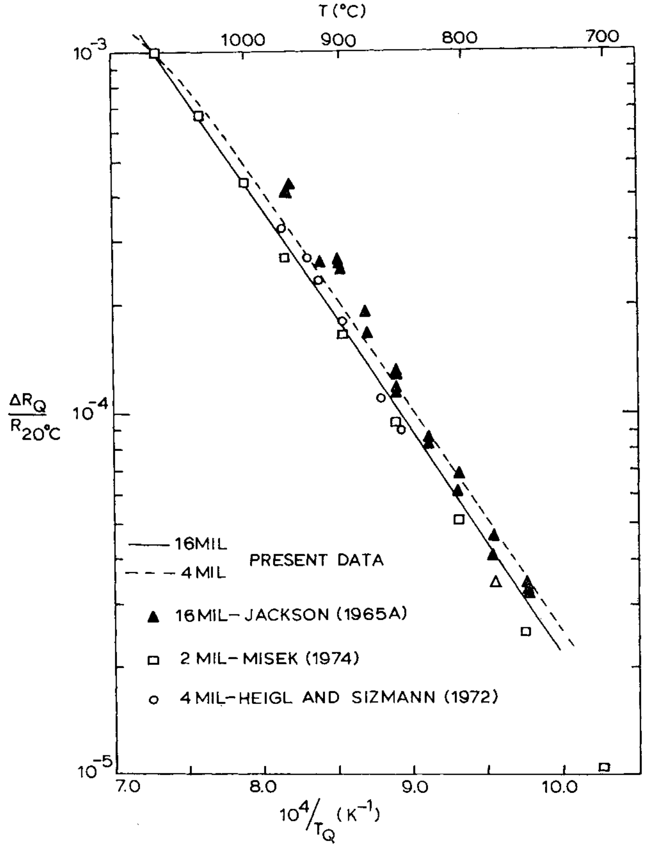
As is seen from fig. 2, the lower inferred values of $E_f^{\text{eff}}$ result from a clear systematic difference in slope between the present 16 mil data and Jackson's. To investigate which results are better supported by other quenching data, the present data for both 16 mil (solid line) and 4 mil (dashed line) diameter wires are compared in fig. 3 with Jackson's data for 16 mil diameter wires (filled triangles)‡, Misek's data for his purest 2 mil diameter wire (open squares), and Heigl and Sizmann's data for their purest 4 mil diameter wire (open circles). To convert published data from $\Delta\rho_Q$ to $\Delta R_Q/R_{20°C}$ for Pt, $\rho_{20°C} = 10{\cdot}3\ \mu\Omega$ cm was used (Meaden 1965).

† Any such increment would not be present in 4 mil wires, which were never quenched in water, and would be of lesser importance in 10 mil wires, where air quenches were normally used to determine the lowest-temperature data (see e.g. fig. 1).

‡ The triangles were determined from raw data kindly supplied by Dr. Jackson. The magnitudes of these data differ from those indicated in fig. 1 of Jackson (1965 a), apparently because of an error in calculating the resistivity of the sample.

If the data shown in fig. 3 are accepted at face value, then both Misek's data and Heigl and Sizmann's appear to support the present results better than Jackson's : both agree better in magnitude, Misek's data agree better in slope ; and Heigl and Sizmann's data cover too narrow a temperature range to give a reliable slope. Moreover, single data points obtained in the vicinity of 1000°C by Polak (1968), Kopan (1965), Schumacher *et al.* (1968), Bradshaw and Pearson (1956), Bacchella, Germagnoli and Granata (1959) and Ascoli, Asdente, Germagnoli and Manava (1958) all fall below Jackson's data and therefore tend to support the present results better than his. These additional points were omitted from fig. 3 in the interests of clarity.

Fig. 3




Comparison between the quenched-in resistivities obtained in the present work and those obtained by Jackson, by Misek, and by Heigl and Sizmann.

On the other hand, in view of the variations in magnitude of the quenched-in resistivity from sample to sample seen in fig. 2, these arguments cannot be considered conclusive. On the basis of these variations it could be argued that the apparent agreement in magnitude is fortuitous, and that the lower slopes occur as a result of systematic errors in the present measurements.

This is the argument Jackson used concerning quench-data published prior to his. In order to investigate this possibility, each of the potential sources of systematic error which Jackson (1965 a) suggested might be important was considered : (*a*) too-high quenching temperatures ; (*b*) too-slow quenching speeds ; (*c*) too-large quenching strain ; and (*d*) too-low purity of samples. None of these possible sources of systematic error seems to apply to the present measurements. Thus†, (*a*) Jackson's criterion for low temperatures was satisfied by quenching from $T_q \leqslant 1000°C$. (*b*) The quench speeds were comparable to, and in some cases faster than, Jackson's. (*c*) Quenching strains were kept well below the $1 \times 10^{-4}$ value which Jackson (1965 b) found to produce no measurable changes in quenched-in resistivity. (*d*) Jackson used as his measure of the purity of a given sample its residual resistance ratio, $\mathrm{RRR} = R_{293\,\mathrm{K}}/R_{4\cdot 2\,\mathrm{K}}$. Table 1 shows that nearly all the samples used in the present work had RRR's larger than his specified adequate value of 3300, and nearly half had larger RRR's than his largest value of 5400. Therefore by Jackson's criterion, nearly all the samples were of purity equal to, or greater than, his. Moreover, examination of fig. 2 in conjunction with table 1 shows that there is no clear correlation between the inferred values for $E_f^{\mathrm{eff}}$ (i.e. the slopes of the lines in fig. 2) and the RRR's of the samples. Thus, if it is assumed that RRR is a reliable indicator of purity, there seems no reason to believe either that the present samples were significantly less pure than Jackson's, or that impurities were the cause of the deviation of the new data from his.

Thus the lower values of $E_f^{\mathrm{eff}}$ cannot easily be attributed to any of the potential systematic errors which Jackson argued might have adversely affected quenching data published prior to his. If the value $E_f = 1\cdot 5$ eV is to be retained, the lower values derived in the present study must be attributed either to vacancy loss during the quench or to systematic errors arising from other sources. Vacancy loss is investigated in the next section, where all the data are analysed in terms of the FBL theory. The possibility of additional systematic errors is considered in the final discussion.

### 3.3. *The variation of quenched-in resistivity with quenching speed : data*

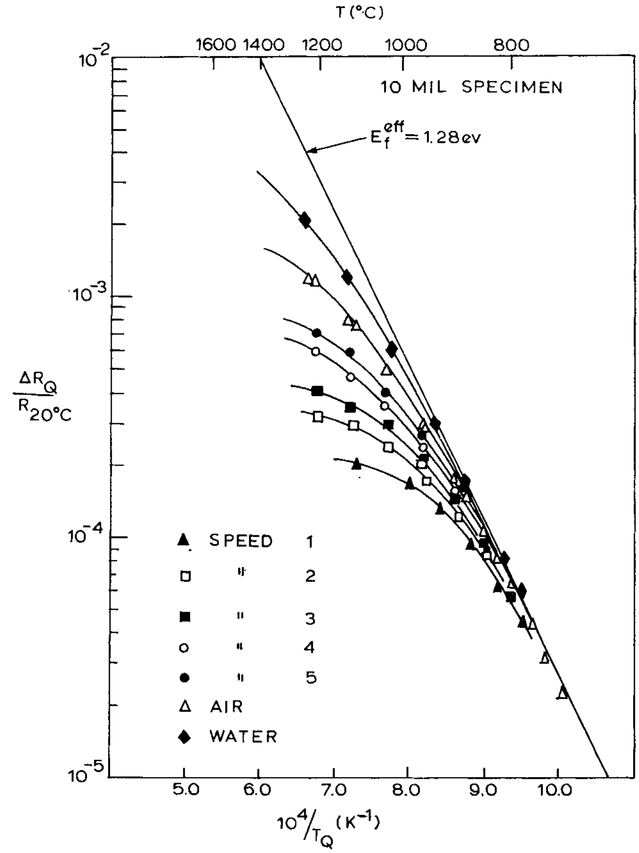
Figure 4 presents data for a single 10 mil diameter sample obtained with water-quenches, still-air quenches, and five different speeds of slowed-air quenches. In order to avoid perturbation of the air-quench data due to changes in sink density produced by liquid-quenching stresses, the water-quenches were carried out after nearly all the air and slowed-air quenches were completed. This latter point will figure in the discussion below.

In addition to the data of fig. 4, consistent sets of data were also obtained for a single 16 mil diameter sample, a pair of 10 mil diameter samples, and a 4 mil diameter sample, in the last case with one proviso which is discussed below. The data for these samples are given in Zetts (1971).

For the 4 mil sample there was a small shift of the data toward lower temperatures midway through the quenching series. When the data from before this shift and the data from after it were plotted on separate graphs

† For a more detailed discussion of these points, see Zetts (1971).

Fig. 4




Resistance quenched into a 10 mil specimen using water, air, and five slow air-quench speeds.

of ln $\Delta R_q/R_{20°C}$ versus $1/T_Q$, it was discovered that the two sets of data could be made to overlap by moving the entire second set horizontally by a fixed amount toward higher temperatures. This procedure yielded an internally consistent set of data. Since this ad-hoc procedure might lead to a systematic bias in the data, it is necessary to treat the results obtained with this sample with some caution. This sample is used only because all the other 4 mil samples experienced even worse data-shifts. Apparently it is very difficult to maintain the sink-density and/or impurity-content of these fine wires constant over a substantial period of time. In agreement with this observation, on attempting to quench 2 mil diameter Pt wires in air and helium gas, the data obtained were too variable to analyse.

### 3.4 *The variation of quenched-in resistivity with quenching speed: analysis*

The only procedure for determining $E_f$ from quenching data taken with finite quench speeds, which can be applied without detailed knowledge of the nature of the sinks at which the vacancies are annihilated, is that of FBL (1965). However, this procedure can be used only when vacancies anneal during the quench to fixed sinks without clustering together. As stated in section IC, the available evidence suggests that vacancy clustering during a quench is not important in Pt. It is therefore assumed that the necessary conditions are satisfied, and the data are examined to see whether they conform to the predictions of the FBL theory.

The fundamental prediction of the FBL theory is that the fractional vacancy-loss during a quench is a function of the single variable $Z = D_q T_q \tau_q$. If for a given value of $E_f$ a particular fractional vacancy-loss is selected, e.g. 50%, then for this fractional loss the data should fit an equation of the form

$$D_q T_q \tau_q = Z = \text{const.} \tag{6}$$

Using eqn. (5) this can be rewritten as

$$D_v \exp(-E_m/kT_q) = Z/(T_q \tau_q). \tag{7}$$

According to eqn. (7), a plot of $\ln (T_q \tau_q)^{-1}$ versus $1/T_q$ should yield a straight line with slope $E_m/k$.

To test this prediction, a value for $E_f$ is first assumed. This value then specifies a straight line on the graph of $\ln \Delta R_q/R_{20°C}$ which passes through the low-temperature portion of the fastest-quench data where there is negligible vacancy-loss during the quench. For each such line, the data determine a series of quench temperatures $T_q$, one for each different quench time $\tau_q$, at which a given fraction of the vacancies is lost during the quench. If these temperatures are plotted in the form $\ln (T_q \tau_q)^{-1}$ versus $1/T_q$ and lie on a straight line, then the theory passes its first test. From the slope of this line a value of $E_m$, to be associated with the value assumed for $E_f$, is determined and it is possible to check whether $E_m + E_f = Q$, as expected from eqn. (2).

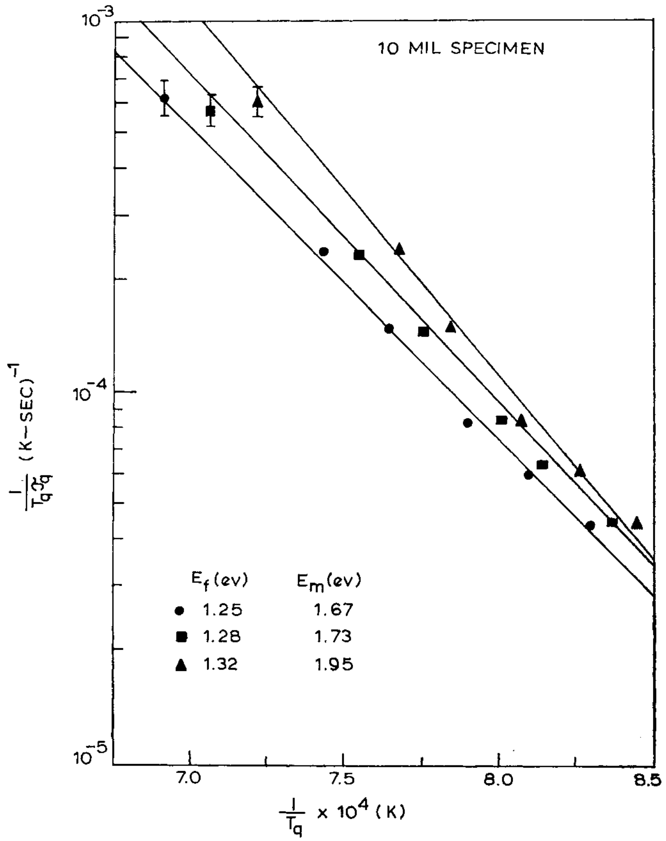
In fig. 5 $\ln (T_q \tau_q)^{-1}$ is plotted against $1/T_q$ for the 50% loss points obtained from the resistivities of fig. 4. The data are consistent with a single straight line. On this graph are plotted the data points obtained with three different assumed values of $E_f$, so as to show how the inferred value of $E_m$ changes when $E_f$ is varied: the change in $E_m$ is two to three times greater than the change in $E_f$. Also, if it is assumed that $E_f \simeq 1{\cdot}26$ eV, as suggested by the low-temperature quench data for the 10 mil diameter samples, then $E_m \simeq 1{\cdot}65$ eV, and

$$E_f + E_m \simeq 2{\cdot}9 \text{ eV}$$

in excellent agreement with the experimental results obtained by tracer self-diffusion.

Similar analyses (Zetts 1971) have also been performed with the other sets of data mentioned above. The results are collected together in fig. 6. For the 10 and 16 mil data, the requirement that $E_f + E_m \simeq 2{\cdot}9$ eV yields $E_f = 1{\cdot}25$–$1{\cdot}3$ eV. For the 10 mil wire this range is consistent with the data obtained below 950°C. For the 16 mil wire it is a little high, but the difference is sufficiently small to be attributable to small strain-induced resistivity increments in liquid quenches, for which no allowance has been made. For the 4 mil data, it is necessary to have $E_f \simeq 1{\cdot}35$ eV for $E_f + E_m$ to equal $2{\cdot}9$ eV. This is at the upper end of the range of values obtained directly from quenches below 950°C.

Fig. 5




Determination of $E_m$ for assumed values of $E_f$ for the 10 mil specimen for which data are shown in fig. 4.

The analysis is concluded by completing the test of the FBL theory in terms of eqn. (7). The ' best values ' for $E_f$ and $E_m$ once established, using the 50% loss points, it is possible to examine whether all the data are consistent with this equation : if, the quench data for various different $T_q$ and $\tau_q$ are plotted together, a single curve should result : that is

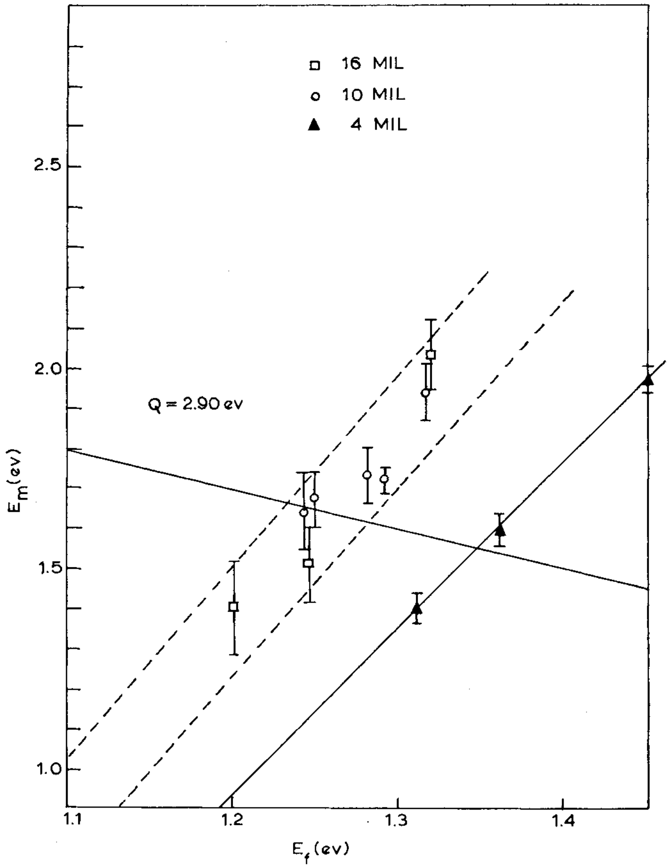
$$c/c_0 = f(D_q T_q \tau_q). \tag{8}$$

Here $c/c_0$ is the fractional concentration of vacancies remaining after a quench from temperature $T_q$ with quench speed $\tau_q$. Since the values of $D_q T_q \tau_q$ commonly run over three or more orders of magnitude, it is convenient to plot

$$c/c_0 = f'[\ln (D_q T_q \tau_q)]. \tag{9}$$

For fixed values of $E_f$ and $E_m$, $f'$ is a function whose shape and position relative to the horizontal axis are uniquely determined by the sample's sink structure and sink density, respectively.

Fig. 6

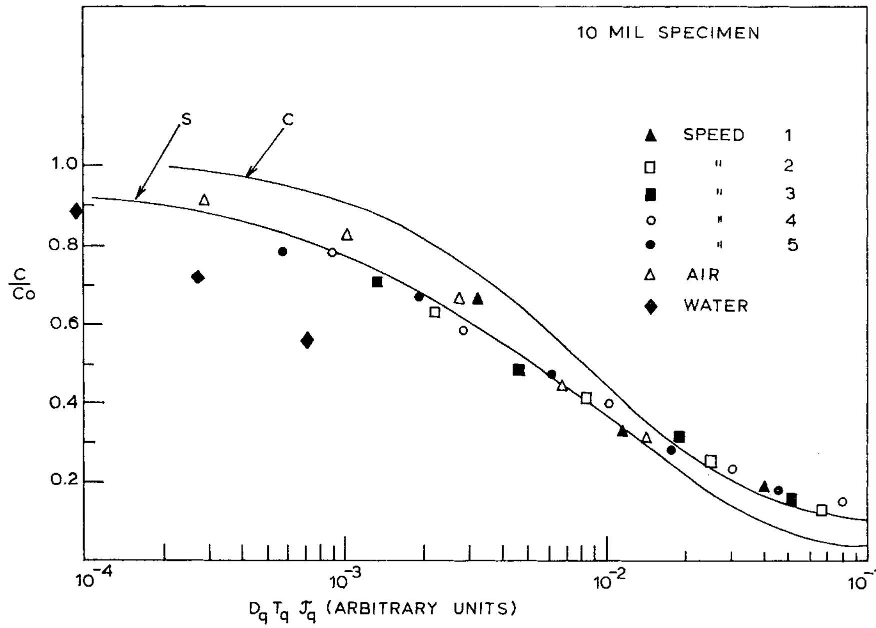



Values of $E_m$ deduced from FBL analysis versus assumed values of $E_f$ for all three specimen diameters.

Figure 7 shows such a plot for the data of fig. 4 assuming $E_f = 1{\cdot}25$ eV and $E_m = 1{\cdot}65$ eV†. Similar plots for the 16 mil and 4 mil data are given in Zetts (1971). In each of these plots the data were observed to fall very nearly on a single curve, in agreement with the predictions of the FBL theory, with the single exception of the water-quench points shown in fig. 7. In order to avoid hydrodynamic quenching strains on the 10 mil sample, this sample was not water-quenched until all the air-quenches were completed. During water-quenching, its RRR fell by 10%. This decrease is attributed to an increase in dislocation density. This attribution provides a reasonable explanation of the fact that the water-quench data fall on a single curve, shifted toward higher sink-density from the air-quench data. Because of this behaviour, water-quench data were *not* used in the FBL analysis of the 10 mil sample.

† An alternative choice of $E_f = 1{\cdot}3$ eV and $E_m = 1{\cdot}6$ eV did not change the qualitative features of this graph.

Fig. 7




Fractional quenched-in vacancy concentration $c/c_0$ versus $D_q T_q \tau_q$ for a 10 mil specimen using $E_f = 1{\cdot}25$ eV, $E_m = 1{\cdot}65$ eV and $Q = 2{\cdot}90$ eV. The line labelled C indicates the form expected for annealing to a uniform distribution of cylindrical sinks. The line labelled S indicates the form expected for annealing to uniformly distributed spherical sinks.

As shown in fig. 7, the data seem to fit better to what would be expected for a uniform distribution of spherical sinks (line S) than to a uniform distribution of cylindrical sinks (line C). In fact, the data fall even less rapidly than would be expected for a uniform distribution of spherical sinks. This is essentially the same result as was obtained previously in studies of Au, Al, and W. In each case this slower fall-off we attributed to non-uniformly distributed subgrain boundaries. Such boundaries would yield a curve which is a superposition of curves for smaller numbers of uniformly distributed spherical or planar sinks, and this curve would fall more slowly, with increasing $D_q T_q \tau_q$, than the solid line S.

From this analysis it is concluded that for each different wire diameter the data are consistent with all the requirements of the FBL theory. Moreover, if allowance is made for a small strain-induced resistivity increment in liquid quenches of the 16 mil samples, then for each wire diameter the range of values of $E_f^{\mathrm{eff}}$ determined from quenches below 950°C contains the value of $E_f$ needed to make the FBL theory consistent with eqn. (2). Finally, taking into account the uncertainties in the data, all three wire diameters yield values of $E_f$ consistent with a single value : $E_f = 1{\cdot}3 \pm 0{\cdot}05$ eV. These results complete the required ' more rigorous test ' of the FBL theory.

On the basis of these results, it is now possible to discuss the assertion of Schumacher *et al.* (1968) that the FBL analysis may yield values of $E_f$ too high because of increasing quenching strains as the quench-speed increases. If this were so, then the highest derived value of $E_f$ would be expected for the sample subject to the largest increase in strain in going from slower to faster quenches. Since the largest increase would occur between slow gas-quenches and rapid liquid-quenches, this would be the 16 mil diameter sample, the only one for which liquid quenches were used in the FBL analysis. However, the 16 mil sample yielded the smallest value of $E_f$, exactly the opposite of what Schumacher *et al.* would have predicted.

There are still two other possible objections to application of the FBL theory to quenched Pt : (1) that neglect of mobile divacancies will lead to incorrect results ; and (2) that the vacancies may be clustering together to form voids during the quench rather than, as assumed in the theory, annealing to fixed sinks. It was argued in the Introduction that the available evidence suggests that divacancies are not important in quenched Pt. Concerning larger clusters, there is no good evidence either way, since all the electron microscope studies of quenched Pt have been made with samples considerably less pure than those used in this work. Impurities act as nucleation sites and thereby greatly increase the number of clusters observed. Probably the best argument in favour of this work is the good agreement of the data with all predictions of the FBL theory, combined with the satisfactory agreement with eqn. (2) found for all three wire diameters.

## § 4. Discussion

The preceding two sections showed that the generally accepted value of $E_f$ for Pt was not reproduced either by fast quenches from low temperatures or by extrapolating data taken with finite quenching speeds to infinite quench speed. For three different wire diameters, fast quenches from below 950°C gave values of $E_f^{\text{eff}}$ ranging from 1·16 to 1·35 eV. From analysis of the variation of quenched-in resistivity with quench temperature and quenching speed values for $E_f$ ranging from 1·15 to 1·35 eV were derived (fig. 6). Combining these results, and allowing for the fact that $E_f^{\text{eff}} \lesssim E_f$, as well as for the possibility of small strain-induced resistivity increments in the thicker wires, a consistent value for all three sample diameters of $E_f = 1{\cdot}3 \pm 0{\cdot}05$ eV was derived. This value is about 15% lower than the accepted value of 1·5 eV first proposed by Jackson (1965 a). In this section possible sources of the discrepancy, and other available information which might allow either of these values to be rejected, are considered.

There are two possible sources for the discrepancy : (*a*) differences in the procedures used to extrapolate data taken with finite quench speeds to infinite quench speed ; and (*b*) systematic errors. The first source seems unlikely, since the extrapolation procedures act in the opposite direction to what would be needed to explain the discrepancy. Jackson extrapolated to infinite quench speed by fitting his data to curves calculated numerically by assuming that the vacancies were annihilated at the cores of dislocations. Since only a small fraction of the initial vacancy concentration is close to a dislocation core, this model would predict a relatively small initial vacancy loss. On the other hand, in the present work a best fit to the FBL analysis was found for vacancies annealing to the surfaces of spherical grains or subgrains. Here a larger fraction of the vacancies is initially near the sinks, leading to a high initial vacancy loss. Given identical data, this model would have yielded a higher $E_f$ than Jackson's. Since this is the opposite of what was found, it appears that (*b*) systematic errors in one or both of the experiments must be the primary source of the discrepancy between the inferred values for $E_f$. As indicated above, and discussed in more detail by Zetts (1971), there are various possible sources of systematic errors in quenching experiments on Pt. However, upon examining the known sources, no convincing explanation for the discrepancy has been found, nor has it been possible to establish who is correct. Moreover, as is shown below, no independent information is available which allows a choice to be made between the two alternative values for $E_f$.

With given values for $E_f$, $Q$, and $\rho_v^{\text{at. fr.}}$ (the resistivity per atomic fraction vacancies) the following properties can be calculated : the vacancy-formation entropy, $S_f$ ; the vacancy-concentration at the melting point, $C_v(T_m)$ ; and the vacancy-motion energy, $E_m$. Table 3 contains the values calculated using $Q = 2{\cdot}9$ eV, and $\rho_v^{\text{at. fr.}} = 5{\cdot}8 \times 10^{-4}\ \Omega$ cm (Berger *et al.* 1973).

Table 3. Comparison between vacancy properties derived from Jackson's data and from the present work.

| | $E_f$ (eV) | $E_m$ (eV) | $S_f/k$ | $C_v(T_m)$ |
|---|---|---|---|---|
| Jackson | 1·5 | 1·4 | 2·5 | $2{\cdot}4 \times 10^{-3}$ |
| Present work | $1{\cdot}3 \pm 0{\cdot}05$ | $1{\cdot}6 \pm 0{\cdot}2$ | $0{\cdot}2 \pm 0{\cdot}5$ | $1 \times 10^{-3}$ |

Of these values, the only one which has been independently estimated from experiment is $E_m$, which can in principle be derived from annealing experiments after quenching, coldwork or radiation damage. Examination of table 1 shows that the available quenching studies tend to favour Jackson's value of 1·4 eV, although several studies are consistent with 1·6 eV. Studies of radiation damage (Bauer and Sosin 1966) and of cold-work (Miura, Takamura and Ogasa 1968) also provide support for Jackson. On the other hand, a critical review of similar studies made over the last decade, especially studies of Au and Al, suggests that this support may be illusory. Because of vacancy–vacancy and vacancy–impurity interactions, annealing experiments usually measure an 'effective migration energy', $E_m^{\text{eff}}$, which often has no simple relation to $E_m$ (Chik 1970). Moreover, different methods of taking and analysing data can lead to different values for $E_m^{\text{eff}}$ (Burton and Lazarus 1970). For both these reasons, the annealing results are not considered particularly damaging to the results obtained in the present work.

Too little is known about $S_f$ and $C_v(T_m)$ to permit the assertion that any of the values in table 3, are unacceptable. It is perhaps worthy of note, however, that $C_v(T_m)$ inferred from Jackson's data is three times larger than has been observed for any other f.c.c. metal.

## § 5. Conclusions

On the basis of the present results it is concluded that the FBL theory of the annealing of vacancies to fixed sinks during a quench gives a good description of the variation of quenched-in resistivity with quench temperature and quenching speed in Pt. On the basis of these measurements and recent measurements by Misek (1974), it is concluded that the vacancy formation energy in Pt may well be lower than the accepted value of 1·5 eV. Taking into account all the data obtained in the present work, and allowing for known possible systematic errors, a best estimate of $E_f = 1{\cdot}30 \pm 0{\cdot}05$ eV results, where the specified uncertainty should be taken as no better than one standard deviation. To determine whether this estimate is correct, it would be helpful to have additional experiments involving techniques other than quenching. Especially helpful would be either direct determinations of $C_v(T)_m$ and $E_f$ after the fashion of Simmons and Balluffi (1960), or measurements of $E_f$ using positron annihilation. It is hoped that the questions raised by this study, as well as the large values of $C_v(T_m)$ inferred above, may encourage such measurements.



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