A TEST OF THE FLYNN, BASS, AND LAZARUS THEORY USING QUENCHED PLATINUM

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ABSTRACT

A TEST OF THE FLYNN, BASS, AND LAZARUS THEORY USING QUENCHED PLATINUM

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We have measured the resistance quenched into platinum wires of various diameters using a variety of quench speeds in order to test the theory of vacancy annealing to sinks during a quench proposed by Flynn, Bass, and Lazarus. Fast-quench data were obtained with 16 and 10 mil diameter wires quenched into water and ice water, using two different liquid quenching systems, and with 4 mil diameter wires quenched in air. Variable-quench-speed data were obtained from: a) water, kerosene, helium gas and air quenches on a 16 mil diameter specimen; b) water, air and slow air quenches on 10 mil diameter specimens; and c) air and slow air quenches on a 4 mil diameter specimen.

The fast-quench data give an effective vacancy formation energy of $E_f = 1.23 \pm .07$ eV for the 16 and

10 mil specimens and $E_f = 1.30 \pm .05$ eV for the 4 mil specimen. These values are substantially lower than the best value of 1.51 eV previously obtained by Jackson. In light of this disagreement, we have examined our fast-quench data with respect to the objections raised by Jackson concerning previous quenching experiments on platinum, but none of these objections were found to be applicable to the data. Certain data shifts observed in this study, as of yet unexplained, may be partly responsible for this disagreement. Otherwise, we have not been able to determine the source of the disagreement.

Analysis of the variable-quench-speed data according to the theory of Flynn et al. show them to be consistent with the theory for a specimen of any one diameter by each of three tests performed. The analysis yields values for the vacancy motion energy E_m which are also found to be dependent upon specimen diameter: $E_m = 1.55$ eV for the 4 mil specimen, and $E_m = 1.65$ eV for the 16 and 10 mil specimens. These values of E_m are substantially higher than those commonly obtained from low-temperature annealing studies by Jackson and others. It is found from the analysis that values of E_f as high as 1.50 eV are incompatible with our variable-quench-speed data and the theory. Because of the disagreement among our data in the values of E_f and E_m for all three specimen diameters, we do not consider that the applicability of the Flynn et al. theory to quenched platinum has been firmly established.

Finally, when the possible effects of quenching strains and vacancy clustering on the data are considered, it is found that any corrections to the data dictated by these considerations would most likely only enhance the differences between our values of E_f and E_m and those obtained by Jackson.

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TABLE OF CONTENTS

TABLE OF CONTENTS (Cont.) Page

LIST OF TABLES

LIST OF FIGURES

I. INTRODUCTION

A. The Vacancy Formation Energy, E_f

The simplest point defect in metals is the lattice vacancy, a site in the perfect lattice from which an atom is missing. It is now well established that substantial concentrations of lattice vacancies are present in thermal equilibrium in metals just below their melting point. The fractional concentration, c_v, of vacancies present at the absolute temperature T is described in terms of a quantity known as the vacancy formation energy, E_f, by (1):

$$c_v = A\, e^{-E_f/kT}. \qquad [1]$$

Here k is Boltzmann's constant, and A is a constant of order unity determined by the entropy increase per vacancy.

Reasonably accurate values for c_v and E_f have now been established for a number of fcc metals. E_f is found to be about 1 eV (electron volt), and c_v at the melting temperature is typically between 10^{-4} and 10^{-3}. The two most important techniques for establishing these values have been: 1) the method of Simmons and Balluffi (2); and 2) quenching. With the method of Simmons and Balluffi, one measures c_v directly. But the measurements are rarely sensitive enough to yield accurate values for E_f. Measurements made after quenching are very sensitive to the presence of vacancies, but they do not measure c_v directly, and can be plagued by systematic errors. Together these techniques have produced reliable results for a number of fcc metals.

Unfortunately, little is yet known about c_v and E_f in bcc transition metals, which have recently been produced in sufficiently pure form to be studied. Because of their high melting temperature, they cannot yet be studied with the Simmons-Balluffi technique (see section B below). This leaves only quenching. But we do not yet know enough about the importance of systematic errors in quenching experiments to be able to say that the results obtained are always reliable. And if we are to interpret data obtained with bcc metals correctly, we must know the conditions under which quenching studies yield reliable data.

The most general theory which has been used to correct for systematic errors occurring in quenching studies is the theory of Flynn, Bass, and Lazarus (3), which deals with the loss of single vacancies to sinks during a quench. However, this theory has never received a truly rigorous test. It is the intent of this thesis to rigorously test this theory with quenching data obtained using platinum, a metal which, according to published data, should be well described by the theory.

In the following sections, we first discuss the Simmons-Balluffi and quenching techniques in more detail. We then describe the method of Flynn, Bass and Lazarus, and review the previous quenching studies on Pt. Finally, we outline the specific goals of this thesis.

B. The Simmons-Balluffi Technique

The Simmons-Balluffi technique involves measurements upon a sample in thermodynamic equilibrium, in which the concentration of vacancies is representative of the temperature at which the measurement is made. In theory, one could determine $c_v(T)$ by measuring any property of a metal in thermodynamic equilibrium which is affected by the presence of vacancies; e.g. electrical resistance, specific heat, sample length, etc. In most cases, however, one does not know with sufficient accuracy just how this property should behave in the absence of vacancies (4). In 1959, Simmons and Balluffi (2) showed that a combination of two particular sets of measurements would allow $c_v(T)$ to be determined, without knowledge of how either property behaved in the absence of vacancies. They showed, for a cubic crystal containing small concentrations of randomly distributed vacancies and interstitials, that

$$c_v(T) - c_I(T) = 3[\Delta L(T)/L_o - \Delta a(T)/a_o]. \qquad [2]$$

Here c_I is the fractional concentration of interstitials (atoms located at positions other than normal lattice sites), and $\Delta L/L_o$ and $\Delta a/a_o$ are the fractional increases in the macroscopic length and microscopic lattice parameter of the metal, respectively, as its temperature is raised from room temperature to the temperature T. L_o and a_o are therefore the values of L(T) and a(T) at room temperature. Since at high temperatures c_I is normally much less than c_v(2), equation 2 can be used to determine $c_v(T)$. If c_v can be accurately measured over a finite temperature range, this technique can be used in conjunction with equation (1) to obtain E_f. From eqn 1 we see that a plot of the natural logarithm of c_v--ln c_v--against inverse temperature--1/T--will yield a straight line with slope $-E_f/k$.

Unfortunately, the use of this technique is presently limited by the sensitivity with which $\Delta a/a_o$ can be measured (about 1×10^{-5}--corresponding to a sensitivity of a few percent of the vacancy concentration at the melting point), and by the difficulty of maintaining high temperatures sufficiently constant and uniform along the specimen to produce reliable data. The second difficulty has limited application of the technique to metals which melt below 1100°C (it has thus not been applied to platinum). The first has limited direct determinations of E_f to very few metals (e.g. Al (g), and perhaps Pb (6), Na (7), and Au (8)). Even in these cases the uncertainty in E_f varies from at least 5% to above 10%. Thus this method has not yet been able to provide accurate values for E_f. However, it has: 1) provided values for c_v at the melting temperature accurate to 5 or 10%; 2) demonstrated unequivocally the existence of vacancies and their dominance at high temperatures over interstitials; and 3) helped to confirm the general validity of other techniques for studying the properties of vacancies, particularly "quenching."

To obtain greater sensitivity in measurements of E_f, it is necessary to turn to other techniques. Presently, the most sensitive method for detecting vacancies involves measuring the electrical resistance of a quenched metal at very low temperatures (typically 4.2K). We now describe this method in detail.

C. Quenching

Quenching involves cooling a metal rapidly from a high temperature to a low temperature at which vacancies are immobile. If the metal can be cooled rapidly enough, such that a substantial fraction of the vacancies initially present in equilibrium are trapped in, then the "quenched-in" vacancies can be studied at low temperatures. In the last 19 years, many studies have served to demonstrate the validity of quenching as an experimental technique for studying the properties of vacancies. It is now clear that, provided sufficient care is exercised, and work is confined to samples of sufficient purity, quenching studies can provide reasonably reproducible results, which yield important information concerning the properties of vacancies.

In principle, the concentration of vacancies retained in a quenched sample could be measured directly using the field-ion-microscope, or a variation of the Simmons-Balluffi technique. If the vacancies can be caused to conglomerate into large clusters, they can also be detected with the electron microscope. In practice, each of these procedures suffers from experimental difficulties, and they have not yet been able to yield reliable quantitative results. Most published studies have involved measurements of quantities which are proportional to the vacancy concentration, particularly the low temperature resistivity of quenched samples. In this case, one assumes that

$$\rho_v = \rho_i c_v, \qquad [3]$$

where ρ_i is the resistivity of a unit concentration of single vacancies. Measurements of electrical resistivity at 4.2K allow fractional vacancy concentrations as small as 10^{-8} to be detected. This corresponds to a sensitivity of better than 0.01% of the vacancy concentration at the melting temperature.

If a specimen could be cooled rapidly enough to trap in all of the vacancies initially present at the quench temperature T_q, then, from equations (1) and (3), $\rho_v(T_q)$ would be given by

$$\rho_v(T_q) = \rho_i A\, e^{-E_f/kT_q} \qquad [4]$$

In practice, even with the fastest attainable quench speeds one usually expects some vacancy loss during the quench; the largest fractional losses occurring for the highest quench temperatures. In this case, the variation of $\rho_v(T_q)$ with T_q would not reproduce eqn (4) exactly, and a plot of $\ln \rho_v(T_q)$ vs. $1/T_q$ would, in general, not yield a straight line. However, one can determine at least a lower limit to E_f by fitting a straight line to the lowest quench temperature portion of the data, where the fractional vacancy loss is smallest. In this case it would be more accurate to describe the slope of this line in terms of an effective formation energy, E_f^{eff}, which may not be equal to E_f. In order to determine E_f, it is necessary to correct for vacancy loss during the quench. In principle, this can be done by quenching the specimen with a series of quench speeds, and then extrapolating the data to "infinitely fast" quench speed. However, the validity of such extrapolations can be affected by two experimental difficulties inherent in quenching; 1) vacancy complexing, and 2) quenching strains.

1) vacancy complexing: Since vacancies in fcc metals are known to attract each other (9), some vacancies will be present in equilibrium in the form of small vacancy clusters. Because of the increasing stability of

these clusters at lower temperatures (10), their number and size are likely to increase substantially during quenching, especially for slow quenches from high temperatures. If the number of vacancies present in the form of clusters becomes a significant fraction of the total, then their presence may affect the experimental results obtained. For example, if the resistivity of a vacancy pair (di-vacancy) differs from the sum of the resistivities of two isolated vacancies, then the total resistivity will not accurately reflect the total vacancy concentration. Also, if small vacancy clusters are more mobile than single vacancies, then vacancy loss during the quench will be increased. These effects cannot be taken into account without detailed knowledge of the properties of small vacancy clusters.

2) quenching strains: If a specimen is strained during the quench, three effects can result: 1) the geometry of the specimen will change, leading to a change in its electrical resistance (a change which has no relation to the presence of vacancies); 2) new defects can be created; and 3) new sinks (annihilation centers for

vacancies) can be created. The occurrence of any of these three effects during the quench would change the resistance of the quenched specimen relative to the value it would have had if no strain had occurred. Unless the magnitude and the effect of any such strain were known, it would be impossible to relate the experimental data to the vacancy concentration at the quench temperature T_q. Fortunately, it appears to be possible, with care and proper experimental design, to keep the effects of quenching strain small.

The same cannot be easily said about the problems of vacancy loss and vacancy clustering, both of which are intrinsic to the quenching process. However, if one has a metal in which vacancy clustering should be negligible (e.g. if the interaction between vacancies is small, so that few clusters form), then one can deal with the problem of vacancy loss. We will discuss how in the section devoted to the Flynn, Bass, Lazarus theory. Before doing this, we digress slightly, to discuss two types of experiments of importance for our later discussion.

D. The Relation of Quenching to Annealing and Self-diffusion Experiments

Thus far, we have discussed only one of the important quantities associated with the presence of vacancies in a metal, namely the vacancy formation energy, E_f. Two other quantities of equal significance are the vacancy motion energy, E_m, which is the energy required for vacancy migration through the crystal; and the activation energy for self-diffusion, Q, which is the energy required for atomic migration through the crystal. Atomic diffusion in the fcc metals is known to occur by means of vacancies. Therefore, if only single vacancies contribute to diffusion, the activation energy for self-diffusion, Q, should equal the sum of the single vacancy formation and migration energies (4)

$$Q = E_f + E_m. \qquad [5]$$

Thus, if one knows any two of the above quantities, one can use eqn 5 to determine the third. Since our primary concern in this thesis is with the determination of E_f, we shall discuss only briefly the methods used for determining E_m and Q. For more detailed discussions we refer the reader to articles by Seeger and Mehrer (4) and by Chik (11).

Estimates of the vacancy motion energy E_m are usually deduced from annealing experiments on quenched samples. In these experiments, one introduces a concentration of vacancies into a metal by quenching, and then raises the temperature of the sample to a region where vacancies become mobile. By studying the manner in which the quenched-in vacancies anneal away, one can determine the activation energy for the annealing process (12, 13, 14). The major difficulty with these experiments is one of interpretation: substantial vacancy clustering is likely to occur during the relatively low temperature anneals. Thus the activation energy determined for such a process will represent an average value for all the mobile entities involved--single vacancies, di-vacancies, etc.,--which, in general, will have different motion energies.

Values for Q are usually obtained from measurements of the diffusion of radioactive tracer atoms through a sample of the same chemical species (tracer self-diffusion). The interpretation of such experiments in terms of eqn 5 may not be straightforward if other mechanisms besides the diffusion of single vacancies through bulk material contribute to the diffusion process. For example, Seeger and Mehrer (4) point out that contributions from di-vacancies or diffusion "short circuits" can lead to values for Q which differ appreciably from $E_f + E_m$. In addition, they suggest that both E_f and E_m may be functions of temperature. In this case, even if diffusion takes place solely by means of single vacancies, eqn 5 would hold only if all quantities were measured at the same temperature. By proper care and experimental design, the problem of "short circuits" can be avoided. Because of the high temperatures at which diffusion experiments are performed, the contribution due to di-vacancies and larger clusters is usually not substantial. The variation of E_f and E_m with temperature has yet to be conclusively demonstrated. For these reasons, it is very likely that eqn 5 will represent at least an excellent approximation to reality for most metals. It should therefore be very useful as a means of correlating the results of quenching experiments (which attempt to measure E_f) with those of annealing and self-diffusion experiments (which attempt to measure E_m and Q, respectively). In the following discussion we shall assume eqn 5 to be valid.

E. The Theory of Flynn, Bass, and Lazarus

While the usual aim of quenching experiments is to trap in the maximum number of vacancies by using the fastest obtainable quenching rates, the possibility of deliberately varying the quench speed in order to obtain further information was originally suggested by Bauerle and Koehler (12). This procedure was later carried out by Mori, Meshii and Kauffman (15), who, using a semi-empirical extrapolatation technique, attempted to compensate for vacancy losses during the quench and thereby obtain a better estimate for the vacancy formation energy E_f. A more rigorous approach to this problem was developed by Flynn, Bass, and Lazarus (3), who solved the vacancy diffusion equation for the case of single vacancies migrating to fixed sinks during a quence in which the specimen temperature decreases linearly with time (linear quench). They found the fractional loss of vacancies during the quench to depend only upon the product $D_qT_q\tau_q$, where D_q is the vacancy diffusion coefficient at the quench temperature T_q, and τ_q is the time for the sample temperature to fall linearly to 0 Kelvin. The importance of this result is that it establishes a relationship between the two quantities E_m and E_f in terms of the experimental data. Given the experimental data and a known value for E_f, the theory determines a unique value for E_m. In this case the sum $E_f + E_m$ can be compared to Q, and agreement would constitute a strong argument for the validity of the theory. This is the test we would like to apply in this thesis. If, on the other hand, neither E_f nor E_m is known, the theory can still be combined with the experimental data and with eqn 5 to yield values for both quantities. However, the assumption of the validity of eqn 5 at the beginning of the process precludes its later use as a test of the Flynn et al. theory. It is this second procedure which has been used in previous applications of the theory to Au, Al, and W. The method of application is as follows.

Experimental data are obtained by quenching the sample over a range of quench temperatures for a series of quench times. For each quench time, the data consist of a series of points lying on a curve extending from the lowest quench temperature to the highest. Figure 1 shows such data for Au (16). Here, the vacancy resistance quenched into the specimen, divided by the specimen's resistance at room temperature, is plotted against the inverse Kelvin quench temperature. The quenching speed was varied by quenching the specimen into four different liquids and in air.

The analysis begins with the empirically verifiable assertion that the smallest vacancy losses should occur for rapid quenches from low temperatures. This can be easily seen in Figure 1, where the three fastest quench speeds yield nearly indistinguishable data for quench temperatures below 600°C. Thus it appears that at these temperatures essentially the equilibrium

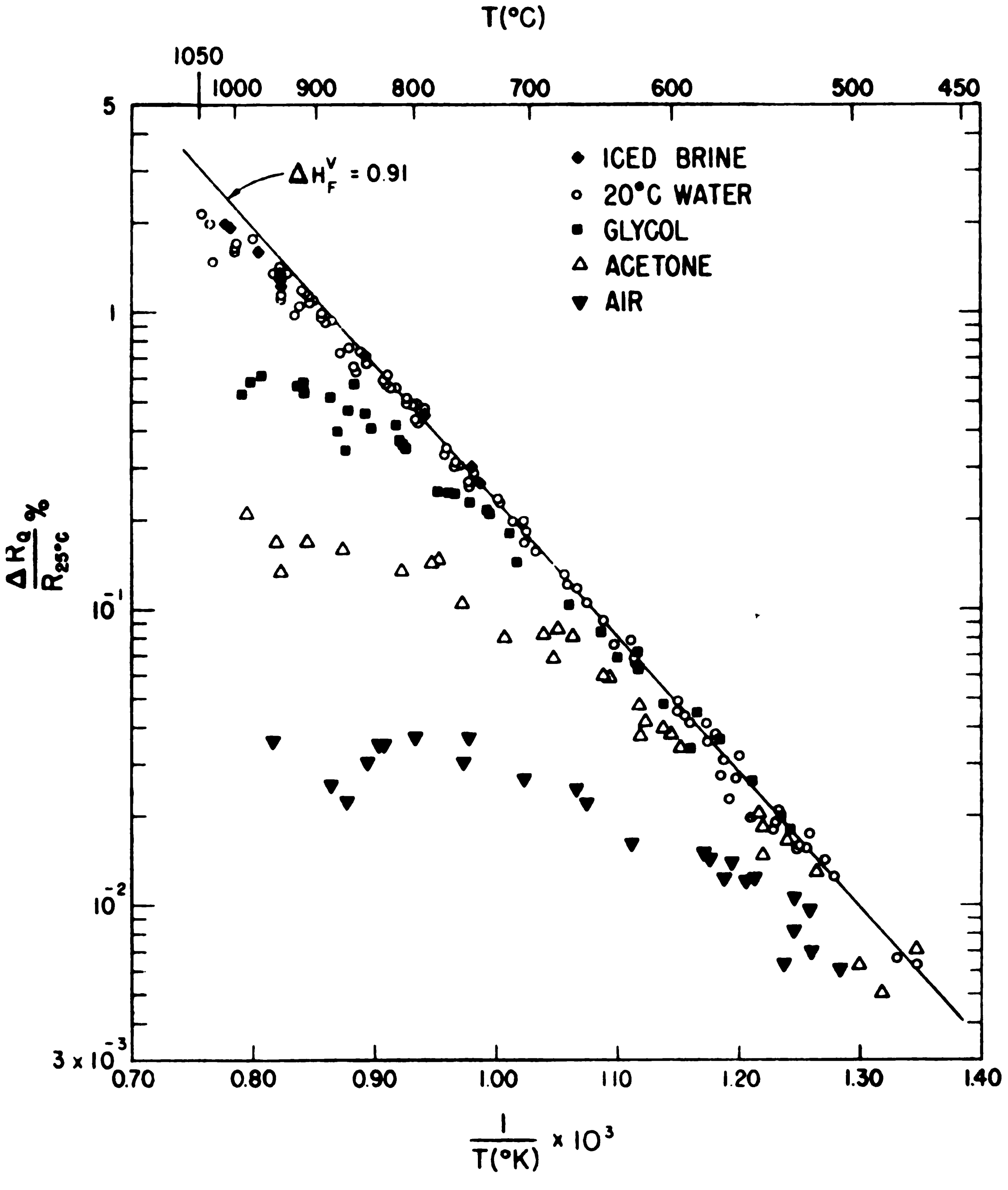

FIG. 1.—RESISTANCE QUENCHED INTO 0.016" DIAMETER GOLD WIRES AS A FUNCTION OF QUENCH TEMPERATURE AND QUENCHING SPEED.

concentration of vacancies is being trapped in during the quench. From eqns 1 and 4 we see that an assumed value for E_f will then specify a straight line in figure 1, which passes through the low temperature, fast-quench data. For each such line, the data determine a series of quench temperatures T_q, one for each quench time τ_q, at which a given fraction of the vacancies are lost during the quench. For quenches characterized by linear cooling curves, the theory leads to the equation

$$D_q T_q \tau_q = Z = \text{Constant} \qquad [6a]$$

or

$$D_q = Z/(T_q \tau_q) \qquad [6b]$$

Since for the motion of single vacancies (4) $D_q = D_o \text{esp}(-E_m/kT_q)$, we obtain,

$$D_o \exp(-E_m/kT_q) = Z/(T_q \tau_q). \qquad (7)$$

Thus a plot of $\ln(T_q \tau_q)^{-1}$ against $1/T_q$ should yield a straight line whose slope is $-E_m/k$. If a straight line is indeed obtained, the theory passes its first test. In this manner a value for E_m is associated with each assumed value for E_f. The "best value" for each quantity is obtained by requiring that their sum equal Q (see eqn 5). Once these values are obtained, the theory can be subjected to its final test by plotting the fractional vacancy loss for all quench times and quench temperatures against the product $D_q T_q \tau_q$. The result should be a single curve containing all of the experimental data.

In the three experiments on Au, Al, and W, the theory passed both the first test and this final test.

In its initial application, to gold (3), the theory yielded the values $E_f = 0.98 \pm 0.02$ eV and $E_m = 0.83 \pm 0.04$ eV, for Q = 1.81 eV. The present consensus is that these are still reasonable values, although the true value for E_f may be slightly smaller, and for E_m slightly larger (17, 18, 19). However, Seeger and Mehrer (20) recently challenged this consensus with a reanalysis of Simmons-Balluffi and Self-Diffusion Experiments. They obtained the values $E_f = 0.87$ eV and $E_m = 0.89$ eV, with Q = 1.76 eV. In order to rationalize the disagreement with the results obtained using the Flynn et al. theory, they suggested that the extrapolation might have suffered from a systematic error associated with increasing quenching strain as the quench speed increased.

In its application to aluminum (21), the theory yielded the values $E_f = 0.71$ eV and $E_m = 0.77$ eV for $Q = 1.48$ eV. Subsequently, the accepted value for Q was lowered to about 1.35 eV (22), a value too low to be reconciled with both the theory and the experimental data.

In its application to tungsten (23), the theory yielded the values $E_f = 3.6 \pm 0.2$ eV and $E_m = 2.5 \pm 0.5$ eV. There presently exist no alternatives to these values.

The most serious deficiency of the Flynn et al. theory is that it does not take into account vacancy clustering during the quench. Recent calculations suggest that such clustering can be very important in metals in which the binding between vacancies is large if small vacancy complexes are substantially more mobile than single vacancies. For example, Perry (24) shows that if the binding energy between two vacancies E_b^{2v} is as large as $E_f/4$, and $E_m^{2v}/E_m^{v} = 0.7$, then for a quench from 500°C and a sink density of 10^8 lines/cm^2, the vacancy loss is about 10% greater for a quenching rate of 10^4K/sec, and 40% greater for a quenching rate of 10^3K/sec than if there were no binding between vacancies. These are certainly significant effects, and may be the reason for the failure of the Flynn et al. theory to yield satisfactory results for aluminum.

F. Previous Studies on Quenched Platinum

The study of vacancies quenched into platinum has been the subject of a number of investigations over the last 15 years. Only two other metals, gold and aluminum, have been studied more extensively. As with gold and aluminum, platinum has several advantages for quenching studies: it does not oxidize appreciably except at temperatures very near the melting point; it is not a strong absorber of gases; and it can be refined to high purity. In addition, because of its rather high melting point (1774°C), a measurable concentration of vacancies can be quenched into it over a larger range of temperatures than with either gold or aluminum.

In the following we shall briefly review the results of previous studies of vacancies in platinum, in order to show the status of the field at the time the present study was begun. In this section we shall take reported results at face value. A more critical and extensive review of these results is given in Appendix C.

Table I summarizes previous work on platinum. Between 1955 and 1961 there were seven studies. The six quenching studies all yielded values for E_f between 1.2 and 1.4 eV. The one study of high temperature electrical resistance and specific heat yielded a value in the vicinity of 1.6 eV.* The quenching and 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, $Q = 2.9$ eV, it is interesting, and perhaps significant, that no single investigator obtained values for E_f and E_m whose sum was this large. Then, in 1964, Misek (30) reported obtaining the values $E_f = 1.24$ eV

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*As suggested in section B, these experiments are usually unreliable. For a discussion of their pros and cons see refs (4) and (41).

TABLE I

REVIEW OF PREVIOUS WORK ON PLATINUM

	E_f ev	E_m ev	$E_f + E_m$ ev	Investigators	Ref.
A.	*Quenching and annealing experiments using electrical resistance measurements.*				
1)	1.2	1.1	2.3	Lazarev and Ovcharenko (1955)	25
2)	1.4±.1	1.2±.1	2.6	Bradshaw and Pearson (1956)	26
3)	1.23	1.42	2.65	Ascoli et al. (1958)	27
4)	1.2±.04	1.48±.08	2.68	Bacchella et al. (1959)	28
5)		1.13		Piercy (1960)	29
6)	1.24	1.7	2.94	Mišek (1964)	30
7)	1.42			Kopan (1965)	31
8)	1.51±.04	1.38±.05	2.89	Jackson (1965)	32
9)	1.46±.02	1.38±.05	2.84	Baumgarten et al. (1968)	33
10)		1.50		Polák (1968)	34
11)		1.33±.05		Schumacher et al. (1968)	35
12)		1.35±.05		Rattke et al. (1969)	36
B.	*Other Methods*				
	E_f ev	Property Measured			
	1.4	Thermoelectric force		Gerstriken and Novikov (1961)	37
	1.6	High-temperature electrical resistance and specific heat		Kraftmaker (1965) and Lanina	38
C.	*Self-Diffusion experiments*				
			Q ev		
			2.96±.06	Kidson and Ross (1957)	39
			2.89±.04	Cattaneo et al. (1962)	40

and E_m = 1.7 eV, whose sum is 2.94 eV. A year later, Jackson (32) obtained the substantially different values E_f = 1.51 eV and E_m = 1.38 eV. He proposed a consistent interpretation of nearly all the existing data based upon the propositions that the value E_m = 1.1 eV (usually obtained from anneals after quenches from high temperatures) corresponded to the motion energy for di-vacancies E_m^{2v}, and that the value E_m = 1.4 eV (usually obtained from anneals after quences 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 the experimental conditions under which their data were obtained (see section IV-D for further discussion of this point). Jackson interpreted his data in terms of a vacancy-vacancy binding energy E_b^{2v} of 0.4 eV, approximately 25% of E_f. Subsequent experiments tended to confirm Jackson's values for E_f and E_m, and they became the accepted values for platinum. Only his estimate for E_b^{2v} was challenged; the most recent estimate being E_b^{2v} = 0.1 eV, as proposed by Schumacher et al. (35).

Qualitative support for this lower binding energy comes from a number of studies which suggest that fewer large vacancy clusters form in platinum than in Al, Cu, or Au. Quenching studies indicate that only a very small fraction of the original quenched-in resistance remains after high temperature quenches and subsequent low temperature anneals. This probably means that the vacancies are annihilating, rather than forming clusters. Also the number of jumps made by a typical vacancy during annealing appears to be much greater than those made in other fcc metals (32). This suggests that the vacancies are traveling all the way to fixed sinks. More directly, electron microscope studies of quenched platinum reveal much smaller clusters formed after quenches from high temperatures and subsequent annealing than in the metals Cu and Al (42, 43). Finally, preliminary results of a Field-ion-microscope study of quenched platinum (44) seem to show few di-vacancies in the quenched material.

At the time the present study began, it thus appeared that the value for E_f lay between 1.45 and 1.55 eV; that the value for E_m lay in the vicinity of

1.4 eV; and that E_b^{2v} was only a small fraction of E_f. From Jackson's results, it appeared that a reasonably accurate value for E_f could be obtained from low temperature quenching studies without resort to extrapolation, since he reported that for quenching temperatures below 1000°C he was able to trap in essentially all of the vacancies initially present in thermal equilibrium.

Platinum thus appeared to be an ideal metal in which to test the Flynn, Bass, and Lazarus model of vacancy loss during a quench, and thereby to obtain a still more accurate value for E_f (and thus also for E_m).

G. The Present Experiment

The present experiment was designed to provide a more rigorous test of the Flynn, Bass, and Lazarus model than had heretofore been made. The experiment was envisioned as follows:

1) Reproduce Jackson's low temperature quenching data, and thus his best estimate for E_f, using the fastest obtainable quenching speeds.

2) Vary the quench speed by quenching wires of different diameters in various liquids, in helium gas, and in air. Agreement between data obtained under these different conditions would tend to refute Seeger's objection that the method of extrapolation was invalidated by quenching strains, since the quenching strains are different for the different quenching methods.

3) Use the value of E_f determined at low temperatures in conjunction with the Flynn et al. theory to determine a value for E_m. Test whether these two values yield results in agreement with the prediction that the data should be a unique function of the product $D_q T_q \tau_q$.

4) See whether $E_m + E_f = Q$. Agreement with this result in addition to all the previous requirements would demonstrate that Perry's objection was not important for platinum--that the effects of vacancy clustering were small.

If all of these conditions were satisfied, we would take it as evidence that the Flynn et al. theory was adequate to describe Pt, and that it was thus worth applying to any metal in which vacancy-vacancy binding was not large.

Unfortunately, despite hard and sustained effort, we were never able to reproduce Jackson's low temperature quenching data. All of our data suggested a value for E_f considerably smaller than 1.5 eV. Therefore in steps 3 and 4 we have used both Jackson's value, $E_f = 1.5$ eV, and our own value $E_f = 1.24$ eV to test the theory. We describe the results obtained below.

II. SPECIMEN PREPARATION AND QUENCHING PROCEDURE

A. Specimen Preparation

All specimens used were hard-drawn 99.999% pure platinum, obtained from the Sigmund Cohn Corporation. The specimens were mounted in holders described in section III and platinum potential leads of the same nominal purity were spot-welded onto them. For specimen diameters of 0.016", 0.010", and 0.004", the potential leads were respectively chosen to be 0.002", 0.002" or 0.0006", and 0.0006" in diameter. The overall length of the specimen varied from 3 to 5 inches, and the gauge length, determined by the separation of the potential leads, varied from 1 to 2 inches. The potential leads were placed as far apart as possible, consistent with good temperature uniformity along the gauge length.

After mounting on the holder, the specimens were resistance-heated in air and given an initial anneal to promote grain growth, to minimize the dislocation density, and to generally remove the effects of drawing. For the 16 mil (0.016") specimens, this originally consisted of one half to one hour at 1600°C, 10 hrs. at 1400°C, and 10 hrs. at 800°C, followed by half hour steps of 100°C each down to 500°C. This anneal produced a residual resistance ratio, R-ratio (the specimen's resistance at 20°C divided by its resistance at 4.2K) of 5000 or greater. It was later found that the high temperature annealing times could be reduced by more than one half with little or no change in the resulting R-ratio.

A similar annealing procedure was initially used for the 10 mil (0.010") specimens and produced R-ratios 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 at 1400°C and a few hours at 900°C, followed by slow cooling. This produced R-ratios in the vicinity of 4000.

An even more restricted annealing procedure had to be used for the 4 mil (0.004") wires. It was discovered that annealing at temperatures greater than about 1250° for more than a few minutes produced quite low R-ratios--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 R-ratios greater than 3000. (This phenomenon is discussed further in Appendix A.)

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 hour at 800°C, followed by slow cooling. For 4 mil wires the anneal consisted of about 1/2 hour at 800°C, followed by slow cooling. Longer anneals at temperatures above 1000°C were sometimes necessary for 16 and 10 mil specimens which had been liquid-quenched from high temperatures. Especially in the latter case, it was not always possible to exactly reproduce the prequench vacancy-free base resistance, which usually showed a small increase.

B. Quenching Procedure

1. Room Temperature Measurements

Prior to quenching one must accurately determine the specimen's resistance at room temperature and at liquid helium temperature (4.2K). For the room temperature measurements the specimen was placed in a large, draft-free plexiglass box and a known current (small enough to avoid heating) was passed through it. The voltage drop across the gauge length was measured on a precision potentiometer. Simultaneously, the air temperature in the box was measured with a mercury thermometer. The resistance at 20°C was then determined from the formula

$$R_{20} = \frac{R(T)}{1+\alpha\Delta T}$$

where $R(T)$ is the resistance at room temperature T, ΔT is the difference between room temperature and 20°C, and α is the temperature coefficient of resistance for platinum ($3.9 \times 10^{-3}/°C$).

2. Liquid Helium Measurements

Before and after quenching, the specimen was immersed in liquid helium, and a known measuring current (usually 1 ampere) passed through it. The value of the measuring current was accurately determined by measuring the voltage drop across a 1Ω standard resistor in series with the specimen. This voltage, and that across the specimen gauge length, were simultaneously measured on precision potentiometers. The measuring currents were chosen to cause no measurable heating of the specimen in liquid helium. To eliminate the effects of slowly varying thermal voltages, reversing procedures were used for both the room temperature and liquid helium measurements.

3. Quench-Temperature Determination

All specimens were resistance heated, and their temperatures just prior to quenching were determined from the ratio $R(T_q)/R_{20}$, where $R(T_q)$ is the resistance at quench temperature T_q. $R(T_q)$ was determined by simultaneously measuring the voltage across the specimen gauge length and across a standard resistor (either 0.01 or 0.001Ω) in series with the specimen. The quench temperature T_q was then calculated from the National Bureau of Standards values for the resistance of platinum as a function of temperature (45).

Before quenching, all wires were examined for temperature uniformity along the gauge length. Since the specimens were visibly glowing at all but the very lowest quench temperatures, any large temperature variations along the gauge length could be easily detected. If such temperature variations were observed, the specimen was either discarded or the positions of the potential leads were changed until a gauge length with satisfactory temperature uniformity was obtained.

4. Quenching Procedure

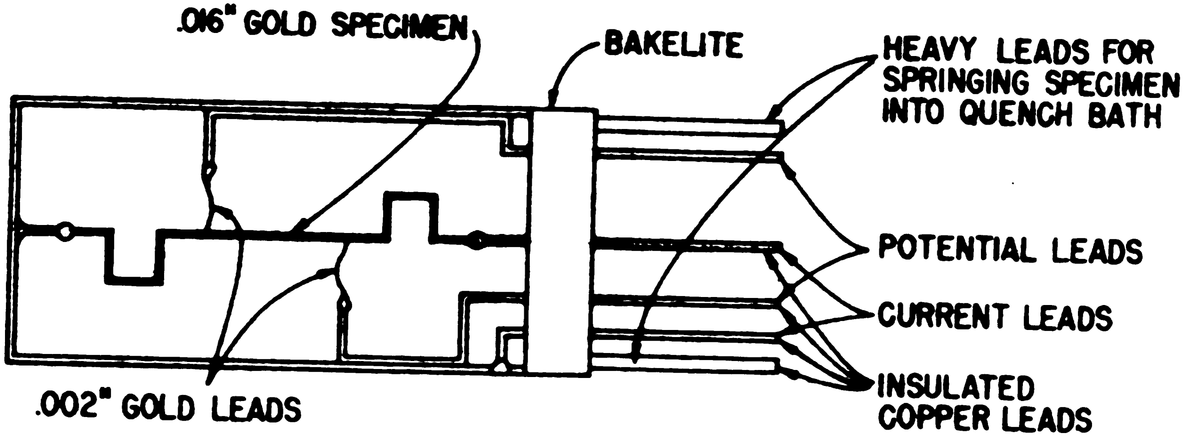
a. The Vacancy-free Base

After the initial anneal, the resistance of the specimen was measured at room temperature and at 4.2K.

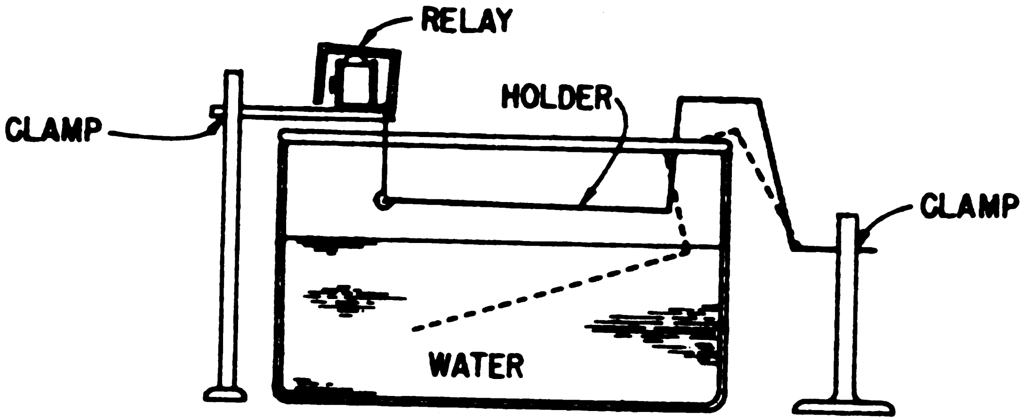
The specimen was then given a few, short, low-temperature anneals and air-quenched several times from 500°C (where the equilibrium concentration of vacancies is too small to be measured). After each series of anneals and/or air quenches, the resistance at 4.2K was measured. Only after a sufficiently stable resistance at 4.2K had been obtained, was the specimen ready to be quenched. The stabilized resistance at 4.2K was used as the "vacancy-free base resistance," R_B.

b. Liquid Quenches

For liquid quenches (water or kerosene) the specimen was mounted in one of the two holders shown in figures 2 and 3, and placed with the axis of the wire parallel to the surface of the liquid and from 1/4 to 1 inch above it. The specimen was resistance heated with direct current and the quench temperature determined from its resistance as described above. With the heating current maintained constant, the specimen was plunged well into the liquid using one of the quenching systems shown in figures 2 and 3. Simultaneously, the voltage



SPECIMEN HOLDER



QUENCHING APPARATUS

FIG. 2.—LIQUID QUENCH SYSTEM I AND ASSOCIATED SPECIMEN HOLDER.

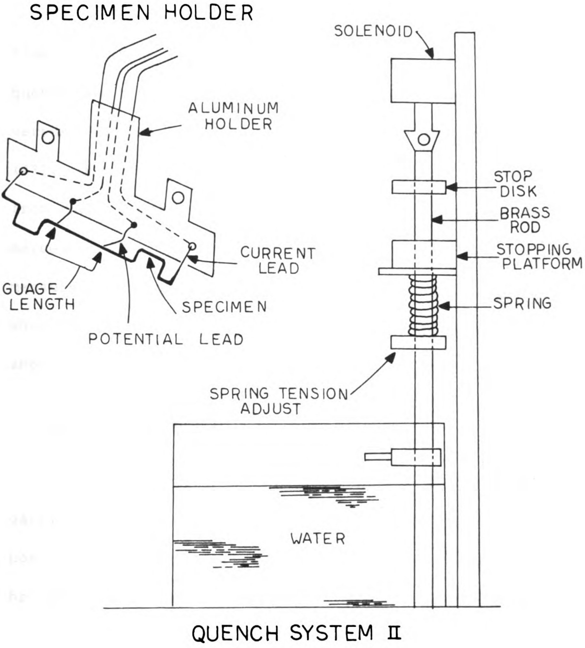


FIG. 3.--LIQUID QUENCH SYSTEM II AND ASSOCIATED SPECIMEN HOLDER.

across the gauge length was displayed on an oscilloscope and photographed. The photographic record of the variation of voltage (i.e. resistance) with time during the quench was then converted to a record of temperature versus time using the N.B.S. resistance-temperature data (45). Quench speeds and quench times were calculated from these converted curves. The specimen was then immersed in liquid helium and the quenched resistance, R_Q, measured. The quenched-in resistance ΔR_Q is then R_Q-R_B, where R_b is the vacancy-free base resistance defined above.

c. Air Quenches

For air quenches (and a few quenches in helium gas), the specimen was placed into the same plexiglass box in which room temperature measurements are made, brought to the quench temperature by resistance heating, and quenched by (1) direct air quenching or (2) slowed air quenching. In the first method, the heating current is abruptly terminated allowing the specimen to cool in a non-linear manner to room temperature. In the second method the heating current is decreased linearly with time as described in section III, causing the specimen to cool more slowly and nearly linearly with time.*

Gas quenching has several advantages over liquid quenching: 1) mechanical quenching strains associated with liquid quenches are virtually eliminated; 2) the cooling curves for air quenches are more reproducible than those of liquid quenches; 3) the nearly linear cooling curves obtained with slowed quenching are easier to characterize for later analysis than the more complex cooling curves obtained with liquid quenches; 4) the quench speed can be varied more continuously than with liquid quenches; 5) the quenching procedure is considerably simplified by elimination of the need for various quenching liquids; and 6) the possibility of specimen contamination by various quenching liquids is removed.

The main disadvantage of gas quenching is that the maximum quench speed obtainable is smaller than that obtainable with liquid (particularly water) quenches.

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*Unfortunately, this technique cannot easily be used to slow down liquid quenches, since upon entering the liquid the specimen cools in spite of the heating current.

Two different attempts were made to overcome this difficulty: 1) a few 4 and 10 mil specimens were quenched by passing a stream of flowing air across them, transverse to the specimen axis, using a device patterned after that of Baumgarten *et al.* (33). This gave initial quench speeds nearly 3 times faster than those of direct air quenches. However, the difficulty of obtaining a uniform temperature distribution along the specimen gauge length limited the usefulness of this technique. 2) We sometimes combined liquid and gas quenches on the same specimen.

With all direct and slowed air quenches, the quench speeds and times were determined by the use of an AC measuring circuit connected in parallel with the DC heating circuit (for details of both circuits see section III-B). After quenching, the specimens were immersed in liquid helium and the quenched-in resistance was determined exactly as with the liquid quenches.

III. APPARATUS AND ELECTRICAL CIRCUITS

A. Specimen Holders and Liquid Quenching Systems

Two types of specimen holder and liquid quenching system were used in these experiments. Both types of specimen holders were used with all three wire sizes, and for both liquid and gas quenches. Quenching system I (QSI) is similar to that originally used by Bauerle for quenching 16 mil gold wires (12). The system and associated specimen holder are shown in figure 2. For the 16 mil wires, 4 to 5 inches of wire was bent into the shape shown in the figure. The half loops on each side of the gauge length were designed to minimize quenching strains within the gauge length as the specimen moved through the liquid. For 10 mil and 4 mil specimens the half loops consisted of short pieces of 16 mil platinum wires spot-welded between the specimen and the copper supports. The thicker loops were necessary to avoid excessive sagging when the smaller wires were heated to high temperatures. The specimen was placed in position over the bath and quenched by opening a relay, allowing the specimen to be sprung into the bath by a springy piece of sheet metal bent into the configuration shown in figure 2.

The second type of specimen holder and associated liquid quenching system (QS II) is shown in figure 3. The system consists of a brass rod, to the bottom of which is attached a teflon holder onto which the metal specimen holder can be mounted for quenching. The top of the rod is attached to the iron core of a solenoid, such that when the current in the solenoid is switched off the specimen is allowed to fall freely, or can be sprung downward into the liquid. The depth of immersion into the liquid is determined by the distance between a rigid "stopping platform" and a brass disk attached to the rod. The position of the disk along the rod can be varied. A foam rubber cushion was placed on the platform to reduce the rapid deceleration at the end of the quench stroke. A coil spring whose compression could be varied by another adjustable brass disk was placed underneath the stopping platform. By varying the spring compression, one could change the velocity of the specimen through the liquid, thereby varying its initial and average quench speeds.

Quench system II produced faster quench speeds than did QS I. It also allowed better control over the specimen's height above the liquid surface, its depth of immersion into the liquid, and its velocity through the liquid.

For QS I, the microswitch activating the relay was also used to trigger the oscilloscope used to photograph the cooling curves. For QS II the scope was triggered by the voltage drop at one of the solenoid leads.

B. Electrical Circuits

1. D. C. Circuits

Since nearly all electrical circuitry used in this experiment has been described in detail in the thesis of R. J. Gripshover (46), only brief mention of the circuitry will be made here, except in referring to apparatus unique to this experiment.

Both alternating current (AC) and direct current (DC) circuits were used. A block diagram of these circuits is shown in figure 4. A and B are the specimen current leads, C and D the potential leads. The DC circuit consisted of three parts: 1) the "measuring" circuit, 2) the "heating" circuit, and 3) the DC potential circuit. The measuring circuit is used to pass a known, constant current through the specimen when measuring its resistance at room temperature or in liquid helium. The heating circuit supplies current to heat the specimen for annealing and quenching. The DC potential circuits are used to measure the voltage drop across the specimen gauge length and to determine the heating or measuring currents by measuring the voltage drop across standard resistors in series with the specimen. S_1 is a DPDT switch used to reverse the current through the specimen. Another DPDT switch, S_2, is used to connect the specimen to either the heating or measuring circuit. The AC circuits are connected to the specimen through small capacitors (about 1 microfarad) and should have no measurable effect on the DC circuits.

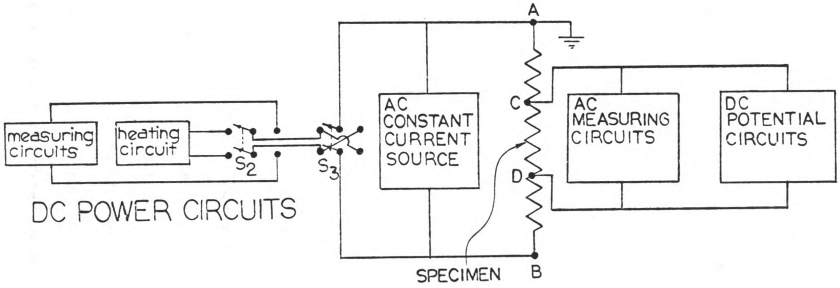

FIG. 4.—BLOCK DIAGRAM OF CIRCUITS.

The measuring circuit consists primarily of a Princeton Applied Research power supply (model TC 602R) and a resistance control box which allows control of a 1 ampere measuring current to better than ±0.0001 ampere. The power supply in the heating circuit is a Kepco model KS-60M, which can operate either as a constant voltage or constant current source. Its output can also be programmed by the use of an external resistance. This application will be discussed in more detail below.

The potentiometers used were a Honeywell model 2780, and a Honeywell model 2779 used in conjunction with a thermal-free reversing switch.

2. AC Circuits

For air and slowed air quenches measurements of the DC potential across the gauge length cannot be used to obtain cooling curves since the DC current either falls rapidly to zero or varies continuously during the quench. Cooling curves were therefore obtained with the AC measuring system described in detail in reference 46. The essential components of this system are shown in the block diagram of figure 5. The AC constant current source (consisting primarily of an audio generator and an operational amplifier) drives through the specimen a current of several milliamperes at 5000 Hz. The AC voltage across the specimen gauge length is then directly proportional to its resistance and independent of the DC heating current. The AC signal is amplified, rectified, and displayed on an oscilloscope, from whose trace the quench speed can be determined in the same manner as with the DC method. Although this system was used primarily for air and slowed air quenches, it also yielded water quench pictures which were indistinguishable from those obtained by direct DC measurement.

The oscilloscope was a Tektronix model 531, used in conjunction with a Fairchild scope camera. For direct air quenches the scope was triggered by the voltage change at point B in figure 4 when the heating current is switched off. For slowed air quenches the scope was triggered by the voltage change at point K in figure 6.

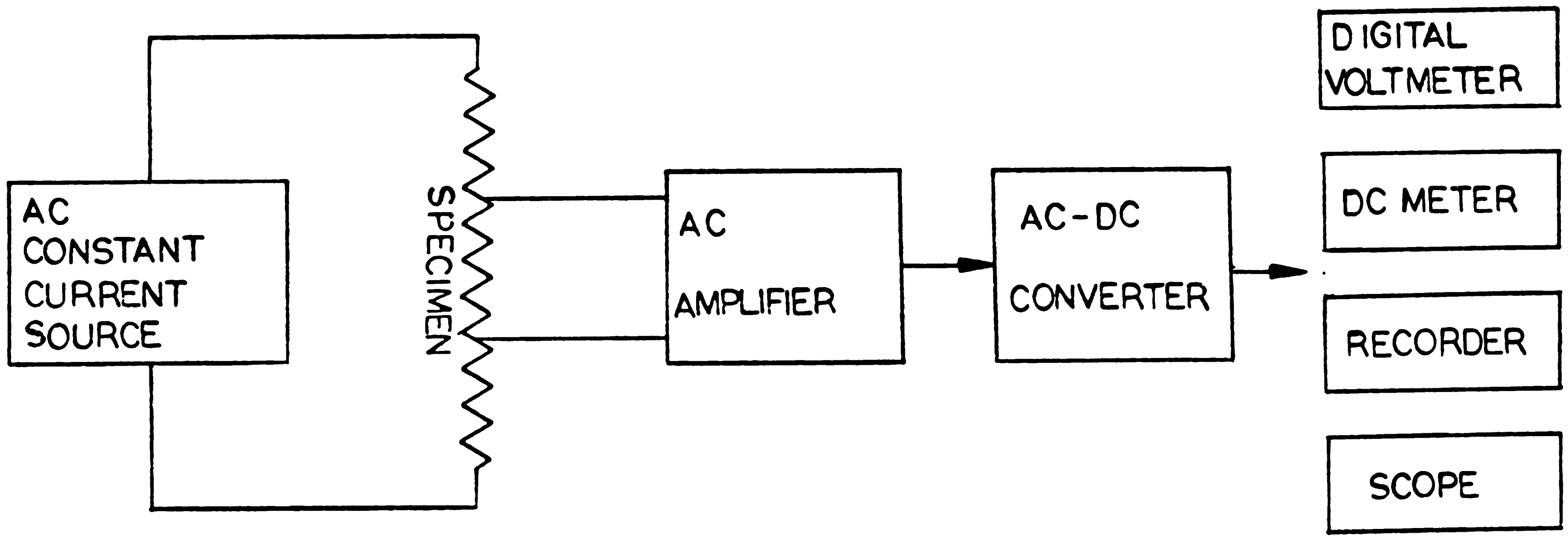

FIG. 5.—BLOCK DIAGRAM OF AC-CIRCUITS

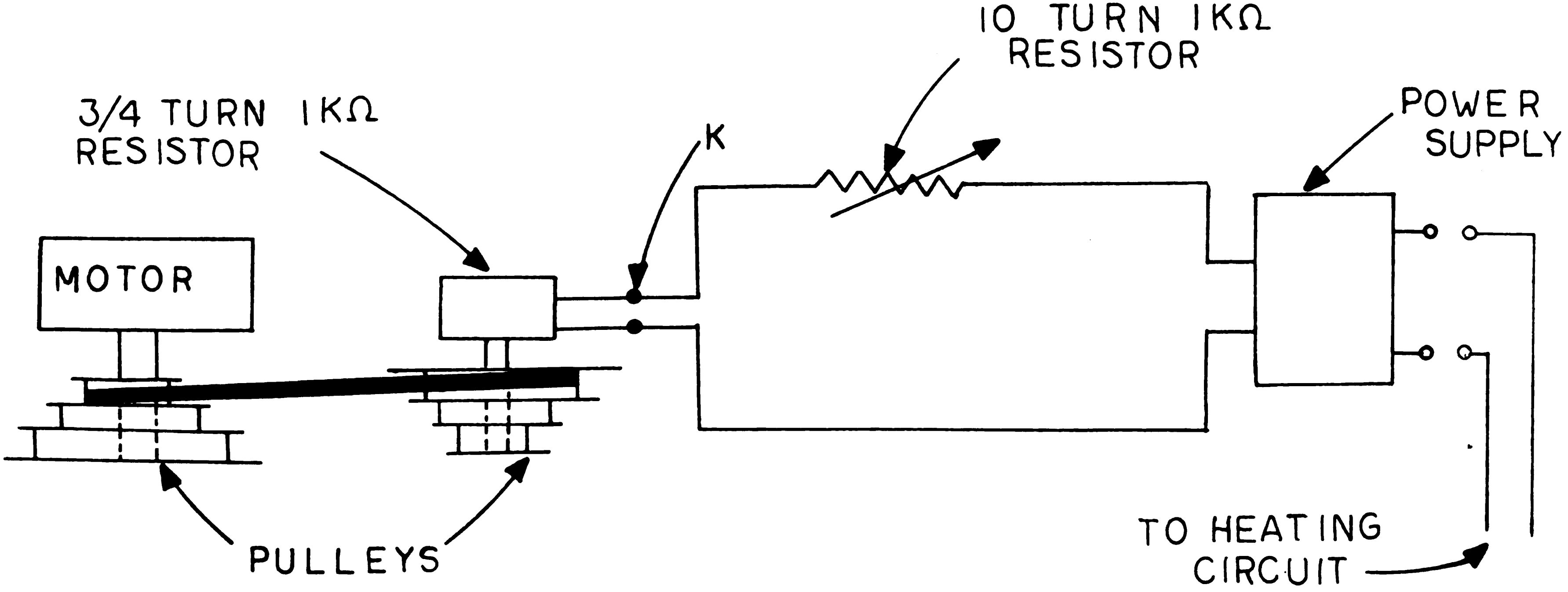

FIG. 6.—SLOW AIR QUENCH CONTROL SYSTEM.

3. Slowed Air-Quench Control System

As mentioned above, the output of the Kepco power supply can be programmed by means of an external resistance. The control system used to obtain slowed air quenches is drawn in figure 6. It consisted of 1 KΩ, 3/4-turn, variable resistor connected by a belt-driven set of pulleys to a Bodine 5.7 r.p.m. motor with forward and reverse drive. The diameters of the pulleys on the motor and resistor axles were chosen to decrease the initial direct air-quench speed by factors of roughly 2, 3, 5, 10, and 15 for the 10 mil specimens and 4, 8, 12, 25, and 50 for the 4 mil specimens. In this control mode, 100Ω of external resistance is needed per volt of the desired power supply output voltage. To allow manual fine adjustment of the pre-quench heating current and to slightly increase the maximum output voltage, a 1 KΩ, manually-controlled, 10-turn helipot was added in series with the motor-driven resistor. The presence of this additional resistance produced a residual heating current in the specimen after the motor-driven resistance had gone to zero, but its effects upon the quenched-in resistance were negligible.

To quench a specimen with this system, the motor-driven resistance was turned to the approximate value necessary to reach a pre-determined quench temperature. The temperature was then set more exactly by manually adjusting the ten-turn 1 KΩ resistor. The motor direction was reversed, and the resistance decreased linearly with time and at a rate governed by the particular set of pulleys used. This caused the specimen's temperature to decrease nearly linearly with time and at a rate approximately equal to that of the resistance decrease.

IV. RESULTS--PART I, FAST-QUENCH DATA

A. Measurements of the Quench Speed

Typical cooling curves for a 16 mil specimen quenched into water with QSI I are shown in figure 7. Here the resistance of the specimen is displayed as a function of time during the quench. Since the resistance of platinum is a nearly linear function of temperature, these pictures are closely equivalent to plots of the specimen's temperature as a function of time. For quantitative evaluation of the quench speeds, the pictures were corrected to representations of temperature versus time using the resistance versus temperature curve for platinum of the N.B.S. (45). This correction produced an increase in the initial cooling rate of approximately 10% for picture "a" and 20% for picture "b." Cooling curves of similar shape were obtained from 16 mil ice-water quenches with QSII, 16 mil water quenches with QSI, and 10 mil water quenches with QSII.

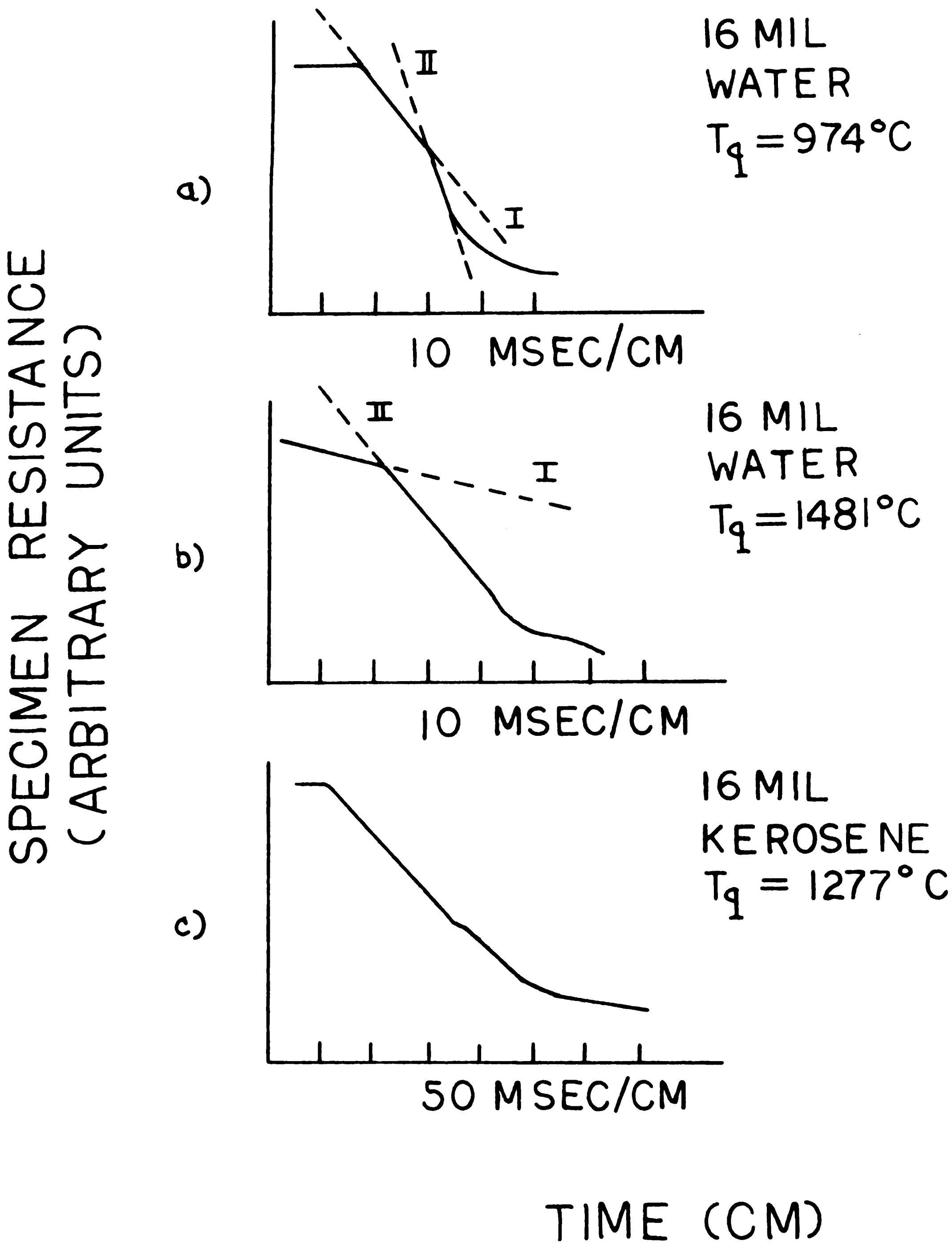

FIG. 7. — COOLING CURVES FOR 16 MIL WIRES QUENCHED INTO WATER AND KEROSENE.

The water quenches can be approximated by two linear quench lines: The initial quench speed, labeled I in figures 7a and 7b, and the maximum quench speed, labeled II in the figures. The maximum quench speed was relatively independent of the quench temperature and varied from 70,000 to 90,000 °C/sec for water quenches with QSII. It was slightly lower for water quenches with QSI. Since our primary concern with the quench speeds is to determine the extent of vacancy loss during the quench, and since the bulk of the vacancy loss occurs during the initial portion of the quench (3), we shall present in detail the data for the initial quench speeds only.

In figure 8, we have plotted the variation of the initial quench speed with quench temperature for 16 mil wires quenched into water with QSI, for 16 mil wires quenched into water and ice-water with QSII, and for 10 mil wires quenched into water with QSII. While we see only a gradual decrease of quench speed with temperatures for quenches with QSI, the behavior of the 16 mil, QSII quenches is quite different. In the latter case, the

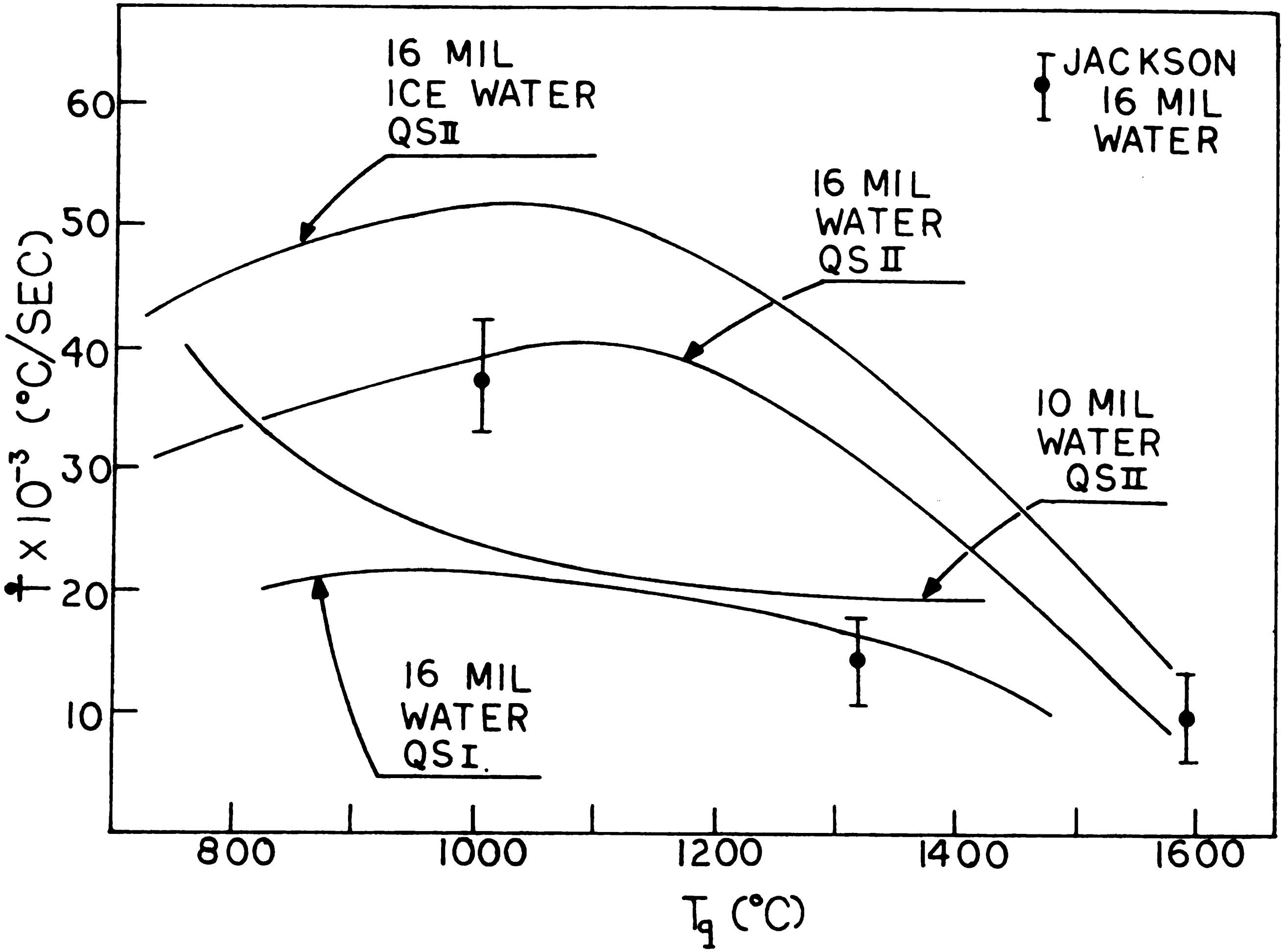

FIG. 8.—VARIATION OF INITIAL QUENCH SPEED, $\dot{T}$, WITH QUENCH TEMPERATURE T_q FOR 16 AND 10 MIL WIRES QUENCHED INTO WATER AND ICE WATER. THREE OF JACKSON'S DATA POINTS HAVE BEEN INCLUDED FOR COMPARISON.

initial quench speeds gradually increase with increasing temperature until about 1100°C, and then fall off rather steeply for the higher temperatures. The lower values for higher temperatures are believed to be caused by an excessive boiling at the specimen's surface (32), shielding it in a layer of vapor and reducing its initial cooling rate until its temperature drops substantially (see figure 7b) and its velocity through the liquid increases somewhat.

The 10 mil quench speeds decrease monotonically with increasing temperature and do not show an intermediate maximum as do the 16 mil wires. We believe this behavior is caused by two opposing factors: 1) the higher initial cooling rates of the 10 mil wires because of their larger surface area to volume ratio and 2) the fact that, to avoid the effects of excessive quenching strains, they were not driven through the water as fast as the 16 mil wires. The curves in figure 8 represent only a best-fit averaging of many quenches. The actual data fell into bands of about ±20% around the curves drawn. The sources of this scatter are twofold:

1) Intrinsic scatter: Even with nominally identical pre-quench conditions, random variations of up to 20% in the quench speeds were observed. These variations arose from factors such as variations in the amount of sag in the wire, and small changes in the specimen's orientation on entering the liquid.

2) Measuring uncertainties: Temperatures and times could be read from the pictures with an accuracy of about 5%, and the uncertainty in the initial quench speed associated with our ability to fit a unique line to the initial portion of the cooling curve varied from 5 to 15%, depending upon the departure from linearity in any particular quench. The effect of both factors on the accuracy of the quench data is discussed below.

A typical cooling curve for a 16 mil wire quenched into kerosene is shown in figure 7c. The kerosene quenches were characterized by a single, linear quench speed of nearly 7000°C/sec which extended for more than two-thirds of the temperature drop. This quench speed was very nearly independent of quench temperature. No kerosene quenches were made with 10 mil wires.

B. The Quenched-in Resistance

Figure 9 contains values for the resistance quenched into three independent 16 mil specimens, quenched into water using QSI. The resistances, divided by R_{20}, the specimen's resistance at 20°C, are plotted on a logarithmic scale against the inverse absolute quench temperature. Division by R_{20} removes the effects of small geometry changes during the course of a specimen's history and allows direct comparison of data for specimens with different gauge lengths and diameters. The error bars shown for some points indicate the uncertainty in the quenched-in resistance associated with differences in the vacancy-free base resistance as measured before and after quenching. When the base resistance changed during the quench, the data points were obtained using a linear average of the two values.

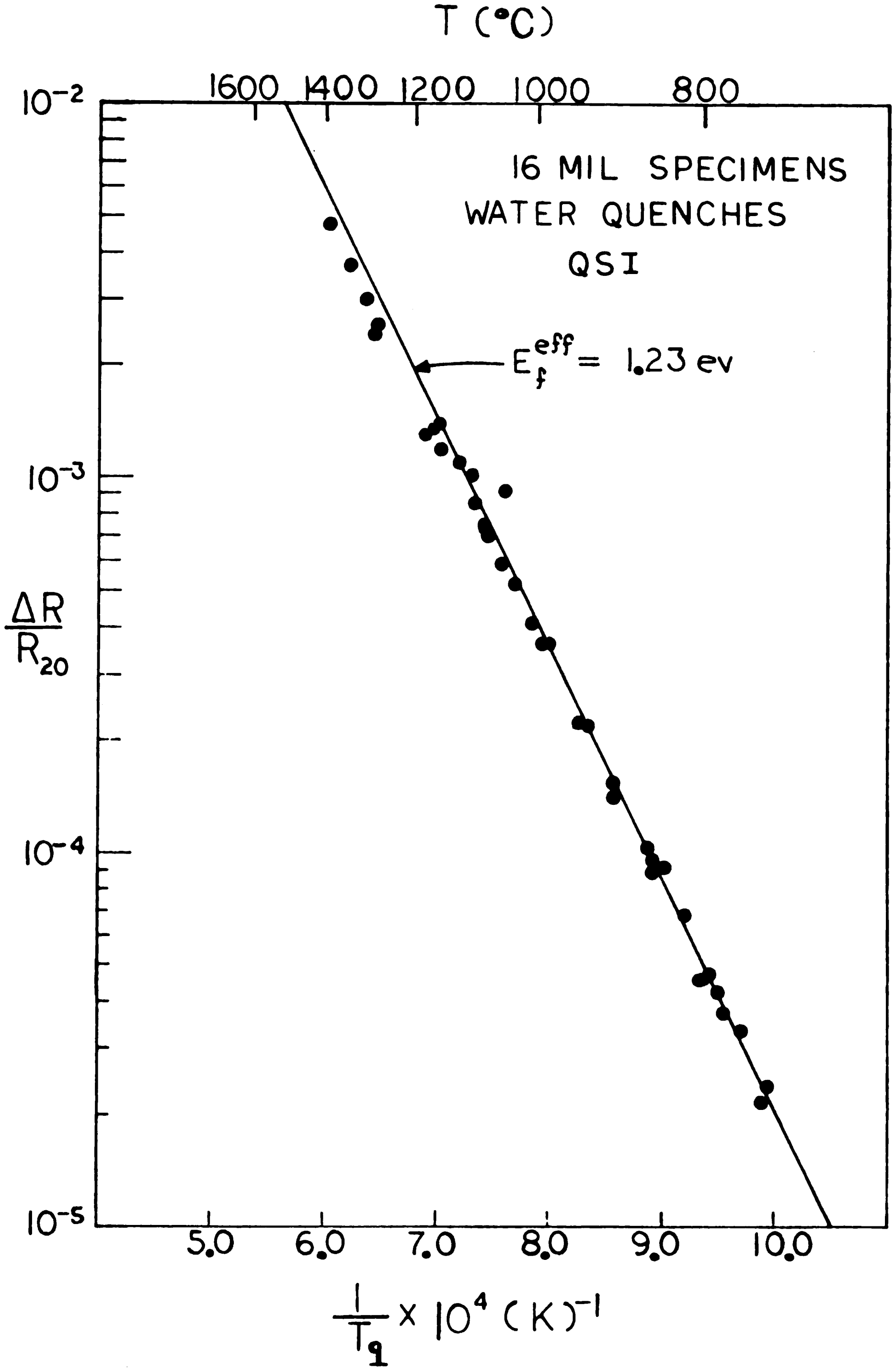

FIG. 9.—RESISTANCE QUENCHED INTO 16 MIL WIRES FOR WATER QUENCHES USING QSI AS A FUNCTION OF INVERSE QUENCH TEMPERATURE.

The line drawn through the data in figure 9 was chosen so as to give the best fit to data in the temperature interval 725 -1000°C (1/T ranging from 10 to 7.85 x 10^{-4}), since, as shown in section VI, in this temperature range only small vacancy loss occurs. To obtain a more accurate estimate of the best-fit line for this temperature interval, the same data were plotted on an expanded scale for the temperature interval 725-1100°C. Both plots yielded an effective formation energy of $E_f^{eff} = 1.23 \pm 0.04$ eV. A 10 mil diam wire water-quenched with QSI showed only slightly larger quenched-in resistances at high quench temperatures and a slightly larger value, $E_f^{eff} = 1.29 \pm 0.03$ eV.

Values for the resistance quenched into two 16 mil diam wires quenched into water using QSII are presented in figure 10. For purposes of comparison with the data obtained with QSI we have included also the best-fit line from the data of figure 9. As can be seen, the quenched-in resistances are somewhat larger, but the slope is slightly lower than that obtained with QSI.

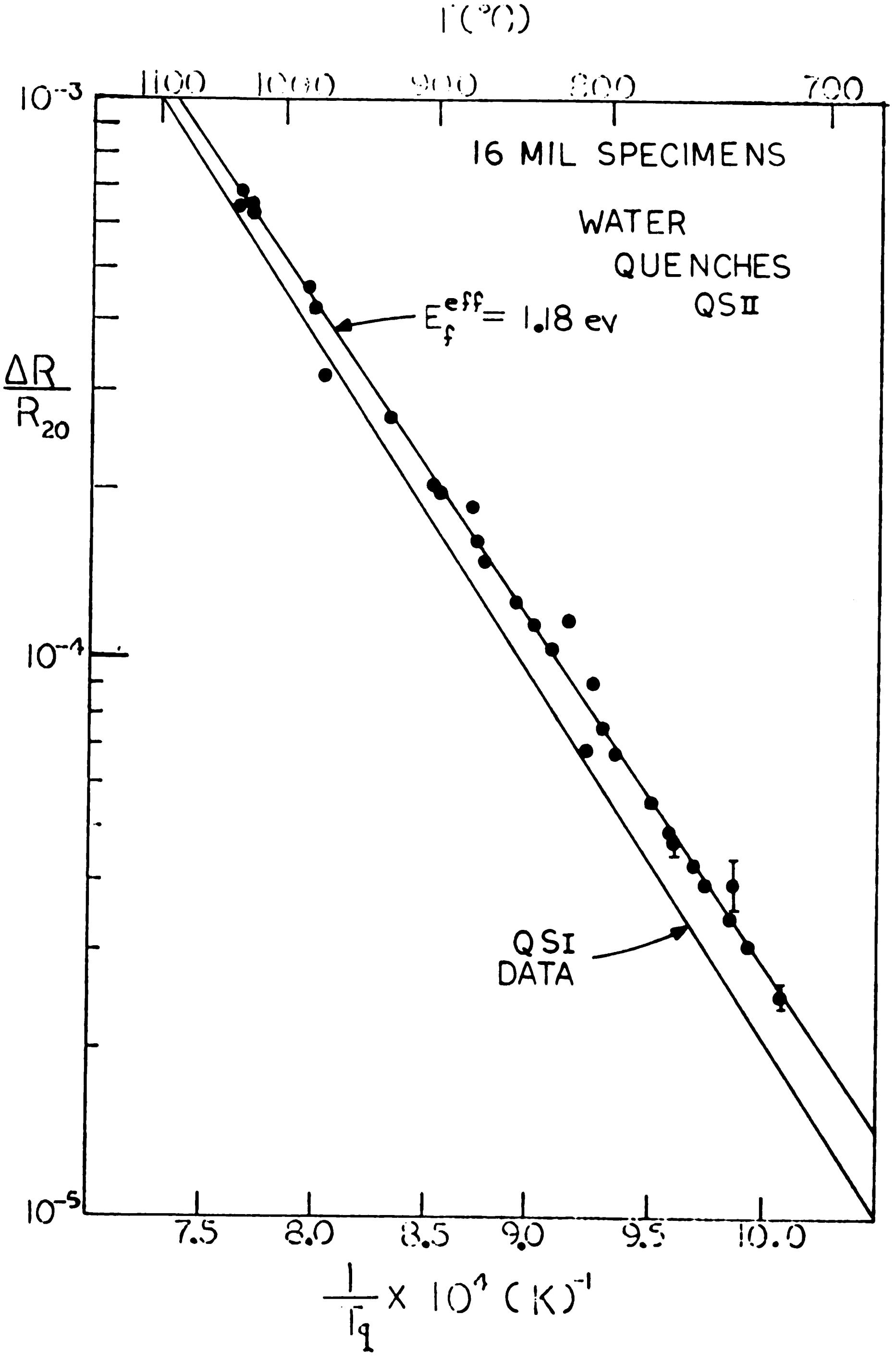

FIG. 10. — RESISTANCE QUENCHED INTO 16 MIL SPECIMENS FOR WATER QUENCHES USING QSII COMPARED WITH THAT OF QSI.

In figure 11 we present data for a single 16 mil diam specimen quenched into both water and ice-water with QSII. Here, the ice-water quenches yield the same slope and only slightly higher quenched-in resistances than those for quenches into water at room temperature. Similar results were obtained with another 16 mil specimen quenched into both water and ice-water.

The low temperature, best-fit lines for water quenches of nine 16 mil specimens are shown in figure 12. In this figure, lines A (3 specimens quenched using QSI) and B (2 specimens quenched using QSII) correspond to the two data lines of figure 10. The lines C through F represent additional specimens quenched with QSII. Line J represents data obtained by Jackson from 16 mil water quenches (32). Notice that it cuts obliquely across the present data and has a considerably higher slope. The data of figure 12 yield values for E_f^{eff} ranging from 1.16 to 1.23 eV. The horizontal shift between lines A and F corresponds to a temperature difference of about 40°C for the same value of the quenched-in resistance. Some possible explanations for these data shifts will be discussed below and in Appendix A.

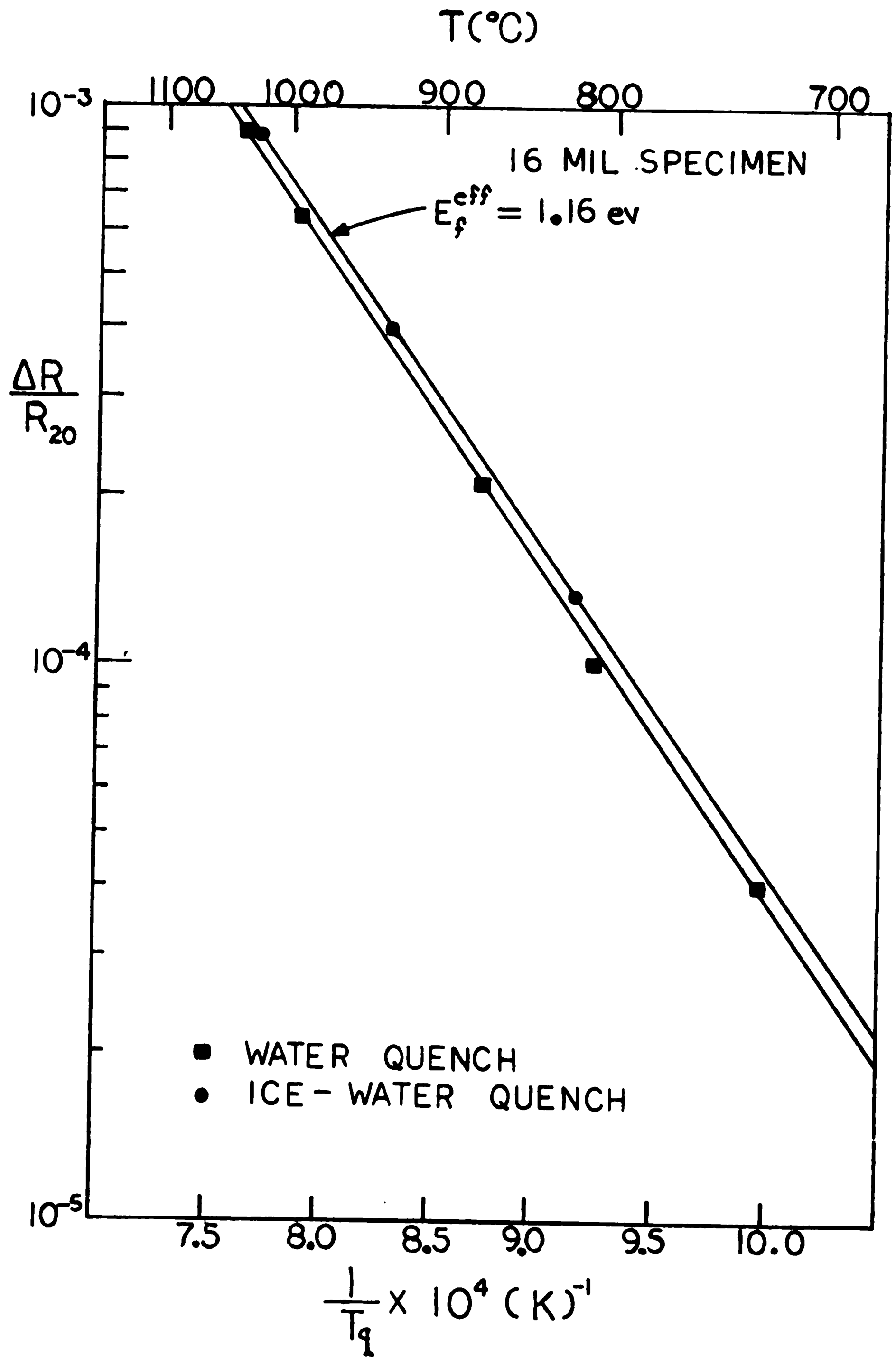

FIG. 11. — COMPARISON OF RESISTANCE QUENCHED INTO 16 MIL SPECIMENS FOR WATER AND ICE-WATER QUENCHES WITH QSII.

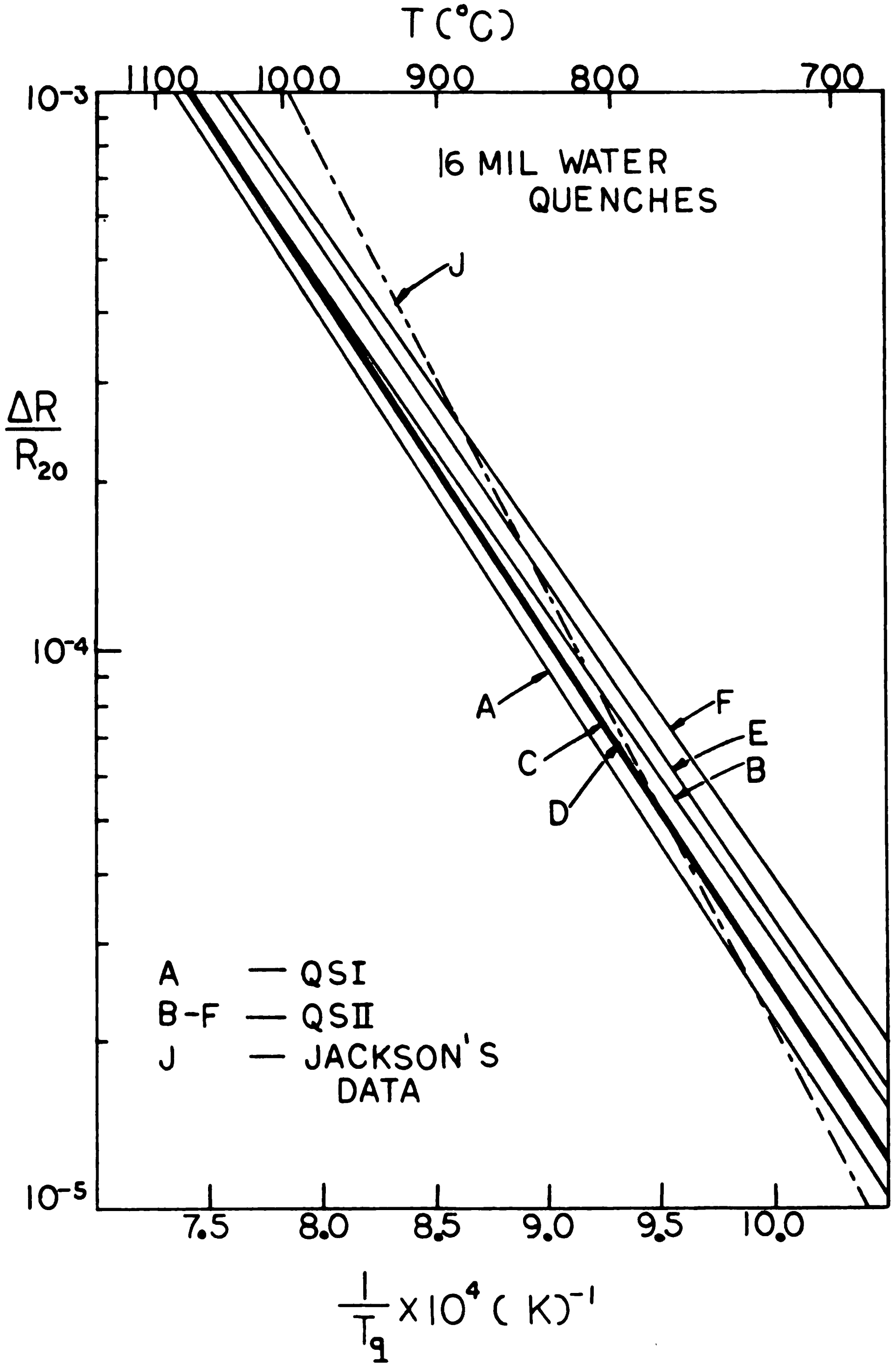

FIG. 12. — COLLECTED QUENCH DATA FOR NINE 16 MIL SPECIMENS QUENCHED INTO WATER USING QSI (LINE A, 3 SPECIMENS) AND QSII (LINES B THROUGH F, 6 SPECIMENS). JACKSON'S WATER QUENCH DATA (LINE J) HAS BEEN INCLUDED FOR COMPARISON.

Water-quench data obtained from three 10 mil specimens using QSII are shown in figure 13. Data for direct air and flowing air quenches of the same specimens are included, since water and air quenches produced comparable quenched-in resistances for quench temperatures lower than 950°C and there is less scatter in the air quench data. These data yield $E_f^{eff} = 1.27 \pm .03$ eV.

We see that in no case are our data consistent with a value for E_f^{eff} much greater than 1.3 eV. This is 0.2 eV or 13% lower than the value of 1.5 eV obtained by Jackson (32). Because of this substantial disagreement, we shall compare in detail in section D the essential elements of both studies. There we shall examine our data in relation to the "systematic errors" which Jackson proposed to explain the difference between his results and those obtained by previous investigators. We ask whether such systematic errors could affect the interpretation of our data. Before doing this, we first consider a number of random and systematic erros which could affect the accuracy of our data.

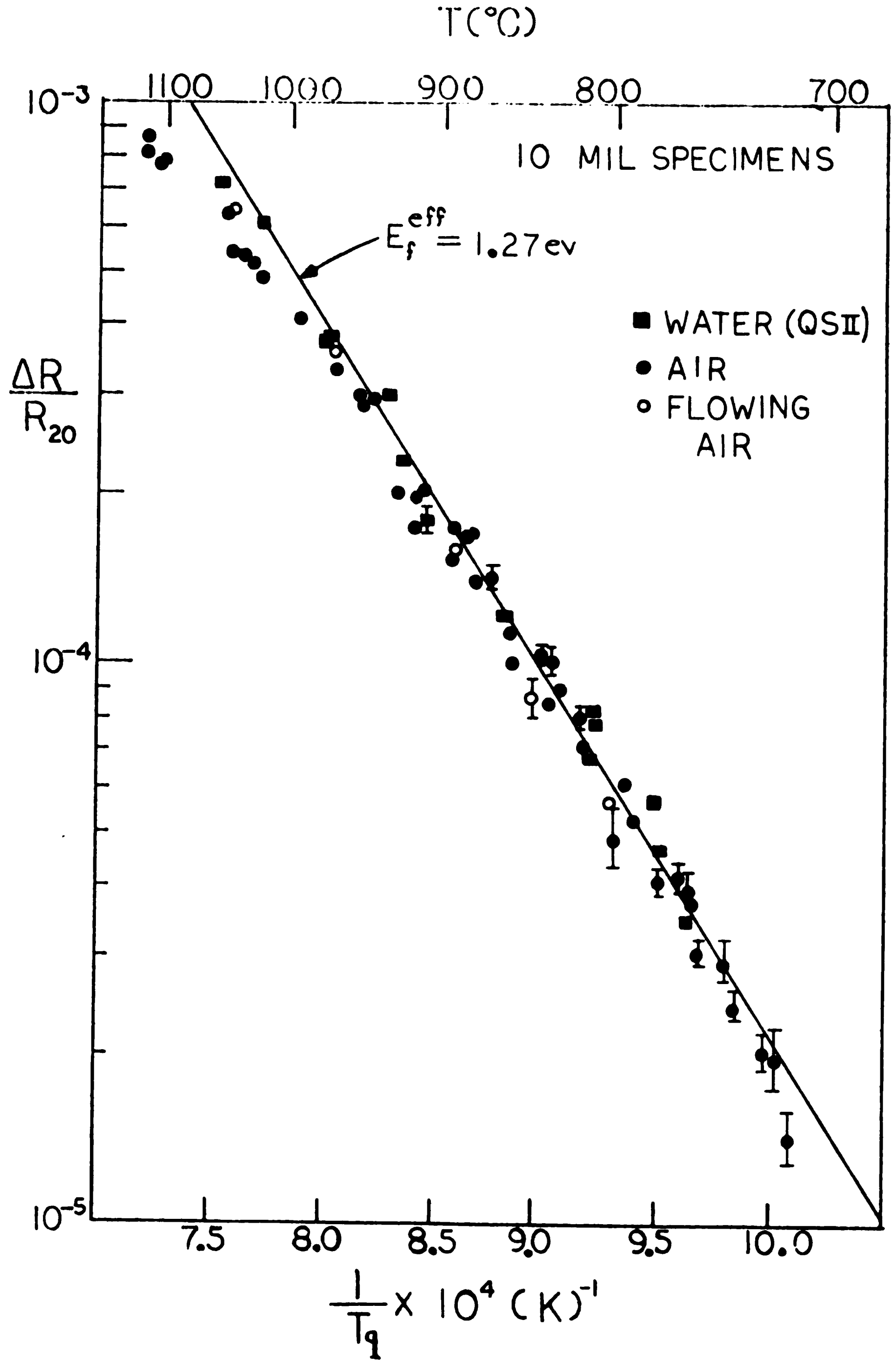

FIG. 13. — RESISTANCE QUENCHED INTO 10 MIL WIRES FOR WATER QUENCHES USING QSII. AIR AND FLOWING AIR QUENCHES WITH THE SAME SPECIMENS HAVE BEEN INCLUDED FOR COMPARISON.

C. Experimental Accuracy

The experimental accuracy of the high temperature quench data is limited mainly by (1) uncertainties in the determination of the quench temperatures. For the low temperature data, additional limitations are produced by: (2) the precision of the resistance measurements in liquid helium, and (3) uncertainties caused by changes in the vacancy-free resistance.

1. The Determination of the Quench Temperature

The accuracy with which the specimen's quench temperature can be determined depends upon: 1) how accurately its room temperature and high temperature resistances can be measured; 2) how constant its average temperature is prior to quenching; 3) how uniform the temperature is distributed across the gauge length; and 4) how well the specimen's resistance ratio at any temperature compares with the values given by the N.B.S. curve. For liquid quenches, there is an additional source of error associated with a possible change in the specimens temperature caused by its fall through the air before entering the liquid.

For all three wire sizes, both the room temperature resistance R_{20} and the high temperature resistance $R(T_q)$ could be measured with a precision of better than 0.1%. These values would produce a maximum uncertainty of less than 2°C in the quench temperature. However, random fluctuations in $R(T_q)$ before quenching were sometimes as large as 0.5%, which corresponds to an uncertainty in T_q of about 5°C and 10°C for quench temperatures of 1000 and 1400°C, respectively. Temperature nonuniformities along the gauge length as large as 100°C can be shown to lead to uncertainties of less than 10°C in the quench temperature. Temperature variations of this magnitude were eliminated by visual inspection of the glowing wires, as discussed in section IIB. The quench pictures show that possible changes in the specimen's average temperature caused by the fall through the air prior to quenching in liquids are no larger than 10°C, the limit of our ability to detect changes from the photographs. Finally, the question of whether the specimen's temperature can be uniquely determined from measurements of its resistance ratio is a complex one, which will be considered in detail in Appendix A.

2. Precision of Resistance Measurements in Liquid Helium

Resistance measurements in liquid helium could be made with a precision of better than 0.1 micro-ohm. This was equivalent to an uncertainty in the quenched-in resistance of about $\Delta R_Q/R_{20} = 3 \times 10^{-6}$ for the 16 mil specimens and $\Delta R_Q/R_{20} = 5 \times 10^{-7}$ for the 4 mil specimens.

3. Changes in the Vacancy-Free Resistance

In general uncertainties associated with fluctuations in the vacancy-free base resistance were no larger than the size of the symbols used in the figures. However, in some cases, variations in the base resistance between consecutive cleansing anneals produced uncertainties in ΔR_Q is large as $\Delta R_Q/R_{20} = 5 \times 10^{-6}$. Error bars are included in the data of figures 9 to 13 to indicate where this occurred.

Finally, we note that the chance of substantial experimental bias arising from the measuring equipment is small. Nearly all of the equipment has also been used in other studies whose results are in reasonable agreement with results obtained in other laboratories.

These sources of uncertainty are sufficient to explain the random scatter observed in the data of figures 9 to 13. However, they are not large enough to explain either the inter-specimen data shifts of figure 12 (i.e. the 40°C effective temperature difference between the two outermost sets of data) or certain intra-specimen data shifts which occurred during the lifetime of some specimens. Discussion of these points is deferred to Appendix A. Likewise, these uncertainties are not capable of explaining the differences between our data and Jackson's, which we discuss next.

D. Comparison with Jackson's Data

In the introduction, we noted that Jackson (32) suggested that the low values of E_f obtained in previous quenching studies on platinum could be caused by certain systematic errors. Specifically, these were: a) the presence of impurities, b) insufficient quenching rates, and c) the effects of quenching strains. We shall now discuss each of these points separately and compare Jackson's values for the pertinent quantitites with our own.

1. Impurities

Jackson reported that he was able to obtain values for E_f as high as 1.50 eV by using the purest possible specimens--R-ratios greater than 5000 (32). In Table II we list values for the initial R-ratios of all 16 and 10 mil specimens used in this study. (The initial R-ratio is that value obtained directly after the long initial anneal given the specimen and before the specimen was quenched). From the table we see that all but one of the 16 mil specimens had initial R-ratios greater than or equal to 4000, and all but two had R-ratios greater than about 5000. In addition the R-ratios of the 10 mil specimens ranged from 3000 to nearly 10,000.

TABLE II

ANNEALING PROCEDURES AND RESIDUAL RESISTANCE RATIOS (R-RATIOS)

Specimen Number	Type of Anneal	R-Ratio	Letter Code
16 mil specimens			
1	a	5470	a - long, high-temperature anneal (10 hrs. or more at 1400°C or higher)
3	a	5600	
6	a	5500	
7	a	1130	
8	b	5270	b - intermediate-temperature anneal (less than 5 hrs. at 1400°C or higher)
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	f - isochronal anneal (100-1000°C)
7	b	3920	
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. It corresponds to line C in figure 2.

Thus, assuming that the R-ratio is a reliable measure of specimen purity, we see that all but two of our 16 mil specimens and all but two of our 10 mil specimens satisfy Jackson's criterion. Moreover, we see no systematic dependence of E_f upon R-ratio for all specimens studied over the full range of R-ratios from 1000 to 10,000. Finally, we have considered the possibility that the specimens become contaminated during the course of quenching, but, as is seen below and in appendix A, the data do not allow one to make a definite conclusion about this hypothesis.

2. Quenching Speeds

Jackson reported that he quenched 16 mil wires into water at maximum cooling rates of 60,000°C/sec or greater (32). These cooling rates are essentially the same as the maximum quench speeds quoted above for water quenches in this experiment. Moreover, we have compared the initial quench speeds--which are a more critical measure of quenching efficiency--obtained in both Jackson's and the present experiments. In figure 8 we have included Jackson's initial quench speeds for three quench temperatures (47). Again, we see relatively good agreement between the two sets of water quench data over the range of comparison. We did not have access to Jackson's quench speed data at the lower quench temperatures, but its absence is not crucial, since we both find that the quenched-in resistance is relatively insensitive to the quench speed for quench temperatures lower than about 1000°C.

Jackson reported that he was able to obtain values of E_f as high as 1.50 eV by quenching rapidly from below 1000°C (32); i.e. for temperatures higher than this he found that the quenched-in resistance varied significantly with quench time τ in the region near $\tau = 0$, and that the values of E_f determined from the high temperature quenches were substantially lower than those obtained from data taken below 1000°C. (Most of the platinum quenching experiments previous to Jackson's had been conducted in the temperature range above 900°C.) Conversely, for quench temperatures lower than 1000°C, Jackson found that the quenched-in resistance was relatively insensitive to even large variations in τ near $\tau = 0$. Returning now to our own data, we note that the quench speeds of various 16 mil specimens quenched with QSII and whose data are included in figure 12 were deliberately varied by the procedure described in section III, A. Variations of up to 40% in the initial quench speeds for quench temperatures up to 1100°C produced no obvious systematic changes in the quenched-in resistance or associated E_f in any of the specimens. Furthermore, in section VI, we show that variations of over an order of magnitude in τ near $\tau = 0$ produce less than a 15% change in the quenched-in resistance for T_q less than 1000°C. Thus, it seems even more unlikely that the differences between our data and Jackson's could be due solely to differences--should they exist--in quench speeds.

By the same reasoning, it is unlikely that the observed shifts in our own data (figure 12) are due to differences in quench speeds. This conclusion is further substantiated when one looks more closely at the data of figure 10. In this figure, we see that line A, corresponding to water quenches done with QSI, yields smaller values of the quenched-in resistance at any quench temperature than those of line B, corresponding to water quenches with QSII. Referring now to the data of figure 8, we see that the respective quench speeds for QSI are lower than those of QSII by nearly a factor of two. However, the slope of line A is, if anything, higher than that of line B. This latter behavior is exactly the opposite that would be expected if the differences in the quenched-in resistance for both lines were caused solely by differences in the quench speeds. The same argument also applies to the water and ice-water data presented in figure 11.

A final and more conclusive argument as to why the data shifts of figure 12 are not associated with differences in quench speed is as follows: A further consideration of the data shifts in figure 12 showed that all specimens quenched with QSII, were also given the shorter, high-temperature, initial anneals, while those quenched with QSI were given the longer anneals. Therefore, to test directly the conjecture that the different annealing procedures were responsible for the data shifts, we quenched an additional 16 mil specimen with QSII, after giving it the longer, high-temperature anneal. The data for this specimen were seen to fall almost exactly on that of line A (previously associated only with QSI quenches), thus substantiating our hypothesis.

Having concluded that these data shifts are probably associated with differences in annealing procedure, we have attempted to formulate an explanation concerning the exact mechanism involved and discuss this in Appendix A. However, as is concluded there, the problem is a complex one, and a complete explanation still eludes us.

3. The Effects of Quenching Strains

In his study of strains in quenched metals (48), Jackson showed that the hydrodynamic strains encountered by thin wires quenched into liquids can produce lower quenched-in resistances than in unstrained specimens at all but the lowest quench temperatures. Such an effect could also produce a lower effective formation energy than in unstrained specimens. To minimize these effects, he used thicker wires (16 mil) than had been used in previous experiments (1.6 to 8 mil) and kept quenching strains smaller than 1×10^{-6}--although he found that quenching strains as large as 1×10^{-4} produced no measurable changes in the final quenched-in resistance in 16 mil wires.

In Appendix B, we have estimated the magnitude of the quenching strains encountered by our 16 mil specimens during water quenches. Except for a few quenches from high temperatures ($T_q \geq 1300°C$), we find the quenching strains to be less than 1×10^{-4}, with most of the low-temperature quenches giving strains of the order of 1×10^{-5}.

E. Summary

In the preceding sections, we have presented data obtained from water quenches on 16 and 10 mil wires, and concluded that our data yield a value of E_f^{eff} of 1.23 ± 0.07 eV. (Low-temperature air quenches with a 4 mil specimen whose data is presented in the next section yield a value of E_f^{eff} of 1.30 ± 0.05 eV, in reasonable agreement with the above value.) We then compared our secondary data (specimen purity, quench speeds, and quenching strains) with the criteria proposed by Jackson and found, in each case, that they appear to amply satisfy these criteria. Also, we have examined the possible sources of error in our data, and found that they too are not large enough to account for the differences between our data and Jackson's. Thus--in spite of the fact that we have attempted to carefully follow Jackson's procedure--we are unable to reproduce his data. Presently, we have no satisfactory explanation as to the source of disagreement between our low-temperature, fast-quench data and Jackson's.

V. RESULTS--PART II, SLOWED QUENCH DATA

A. Quench Speeds

Direct air quenches with specimens of all three diameters, and helium gas and flowing air quenches with 16 mil and 10 mil specimens respectively, all yielded non-linear cooling curves of approximately the same shape. A typical quench curve, obtained from a direct air quench with a 10 mil specimen, is reproduced in figure 14a. Figure 15 shows the variation of the initial quench speed with quench temperature for direct air quenches of the three different wire sizes. Here the initial quench speed was determined from the tangent to the cooling curve, after correction to representations of temperature versus time. For use in the analysis described in section VI, the corrected cooling curves were fit to the form $T(t) = T_q/(1 + t/\tau)$. The τs obtained from this fit were then corrected to an effective linear quench time using the procedure described in section VI. This procedure is subject to somewhat less error than just

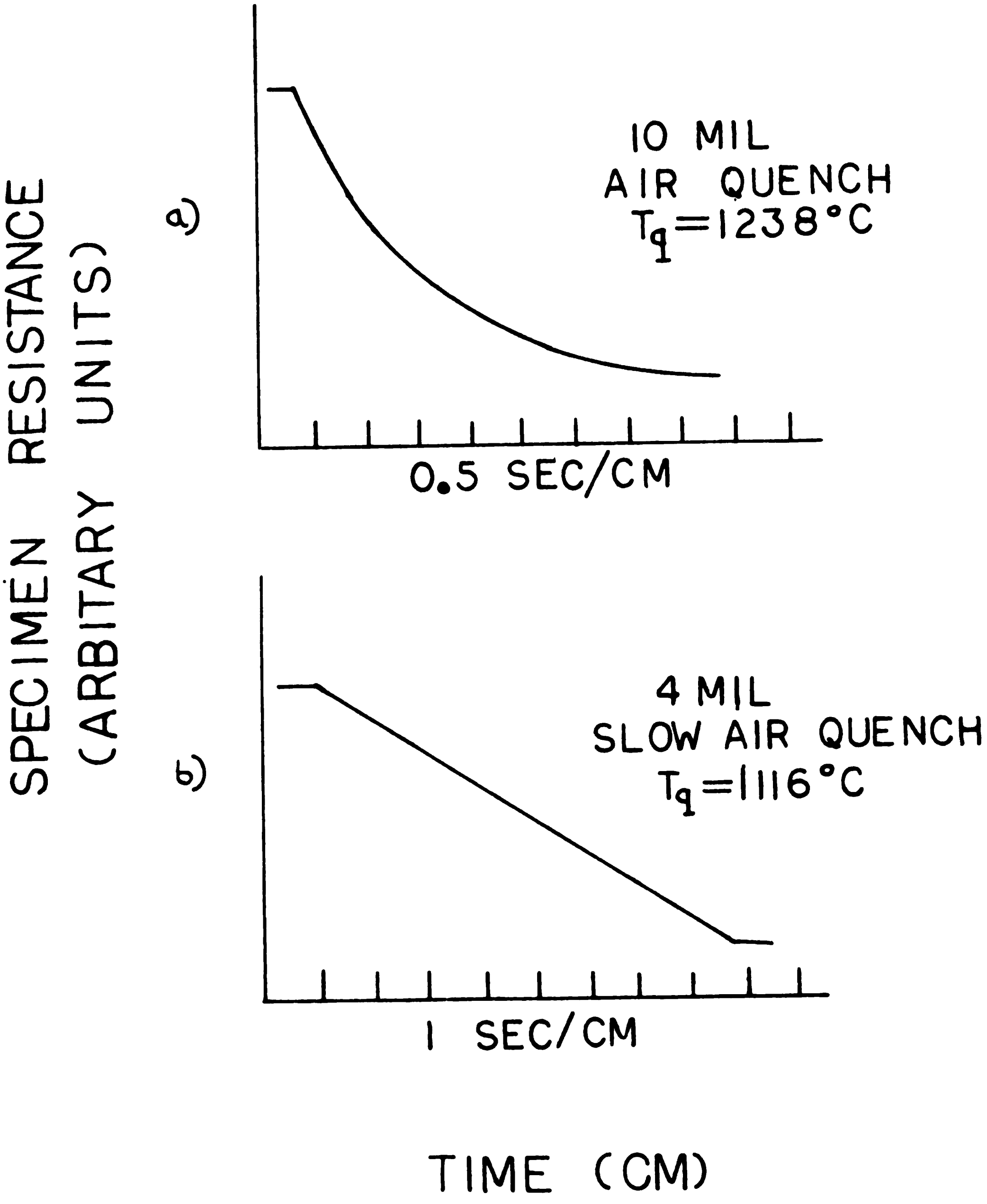

FIG. 14. —COOLING CURVES FOR A) AN AIR QUENCH WITH A 10 MIL SPECIMEN AND B) A SLOW AIR QUENCH WITH A 4 MIL SPECIMEN.

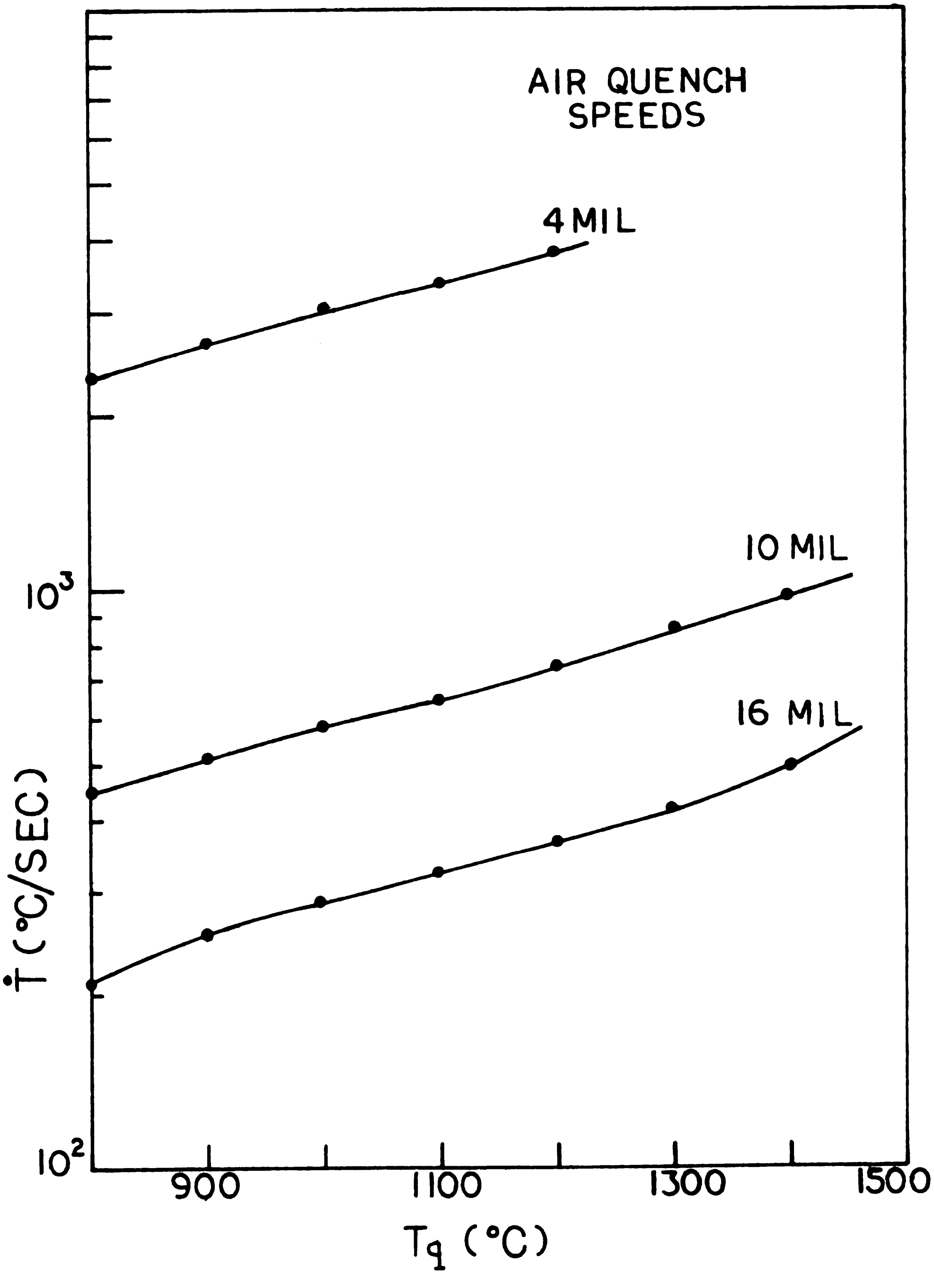

FIG. 15. — VARIATION OF THE INITIAL QUENCH SPEED $\dot{T}$ WITH QUENCH TEMPERATURE T_Q FOR AIR QUENCHES WITH 4, 10, AND 16 MIL SPECIMENS.

taking the tangent to the initial part of the original quench curve.

A typical cooling curve for a slow air quench of a 4 mil wire is shown in figure 14b. These quench curves could be well represented by a straight line extending for about one half of the total temperature drop. This essentially linear behavior characterized all five slowed-air quench settings used with the 10 mil and 4 mil specimens. The dependence of the initial quench speed upon quench temperature for five separate slow-quench settings with a 10 mil specimen is shown in figure 16. A similar temperature dependence was observed for slow air quenches with 4 mil specimens.

B. Quenched-in Resistance

1. 16 mil Data--Slowed Liquid and Gas Quenches

In figure 17 we present data for a single 16 mil specimen quenched into water and kerosene, and in He gas and air. The liquid quenches were with QSII and the gas

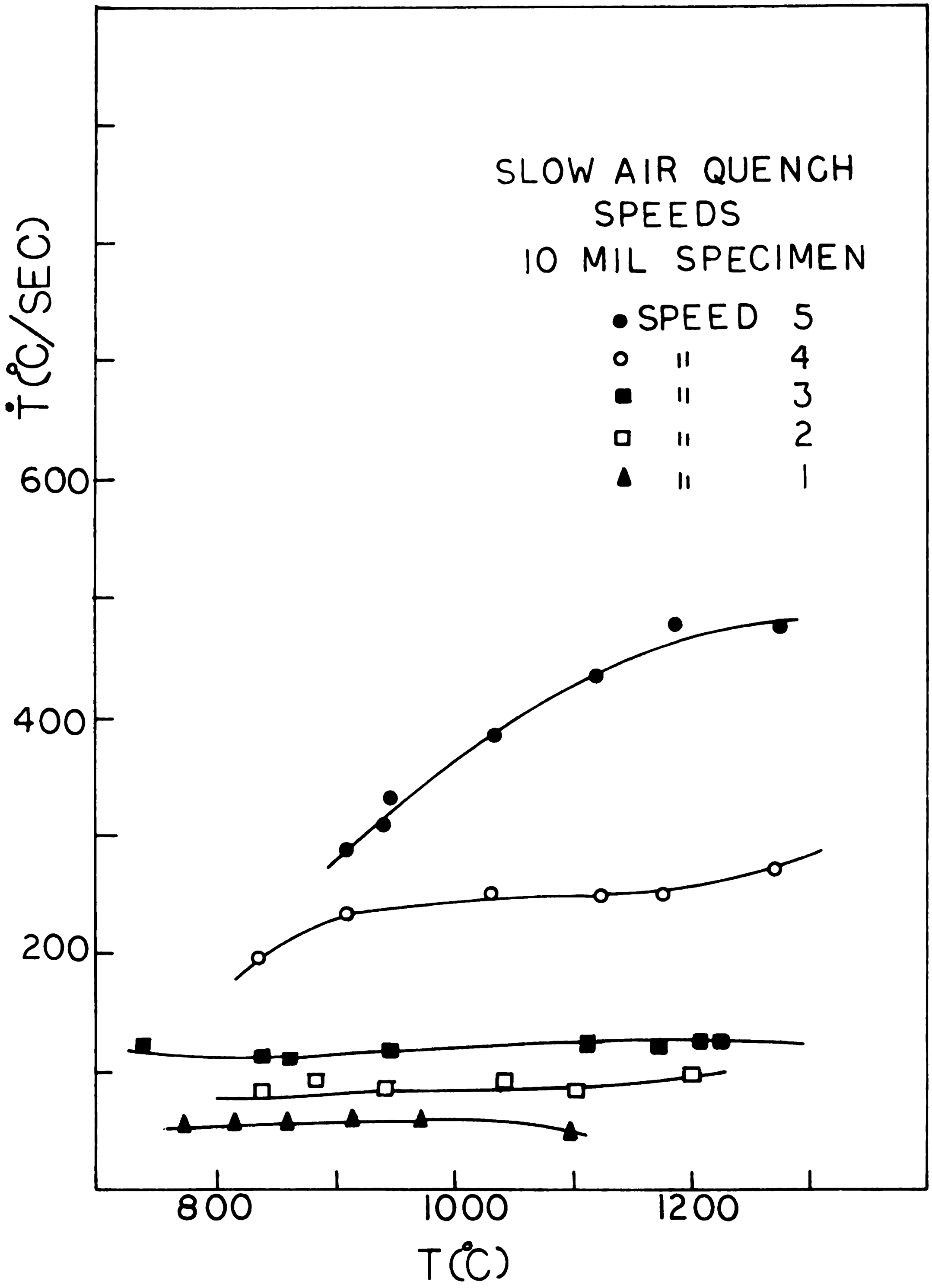

FIG. 16. — VARIATION OF THE INITIAL QUENCH SPEED $\dot{T}$ WITH QUENCH TEMPERATURE T_Q FOR SLOW AIR QUENCHES WITH A 10 MIL SPECIMEN.

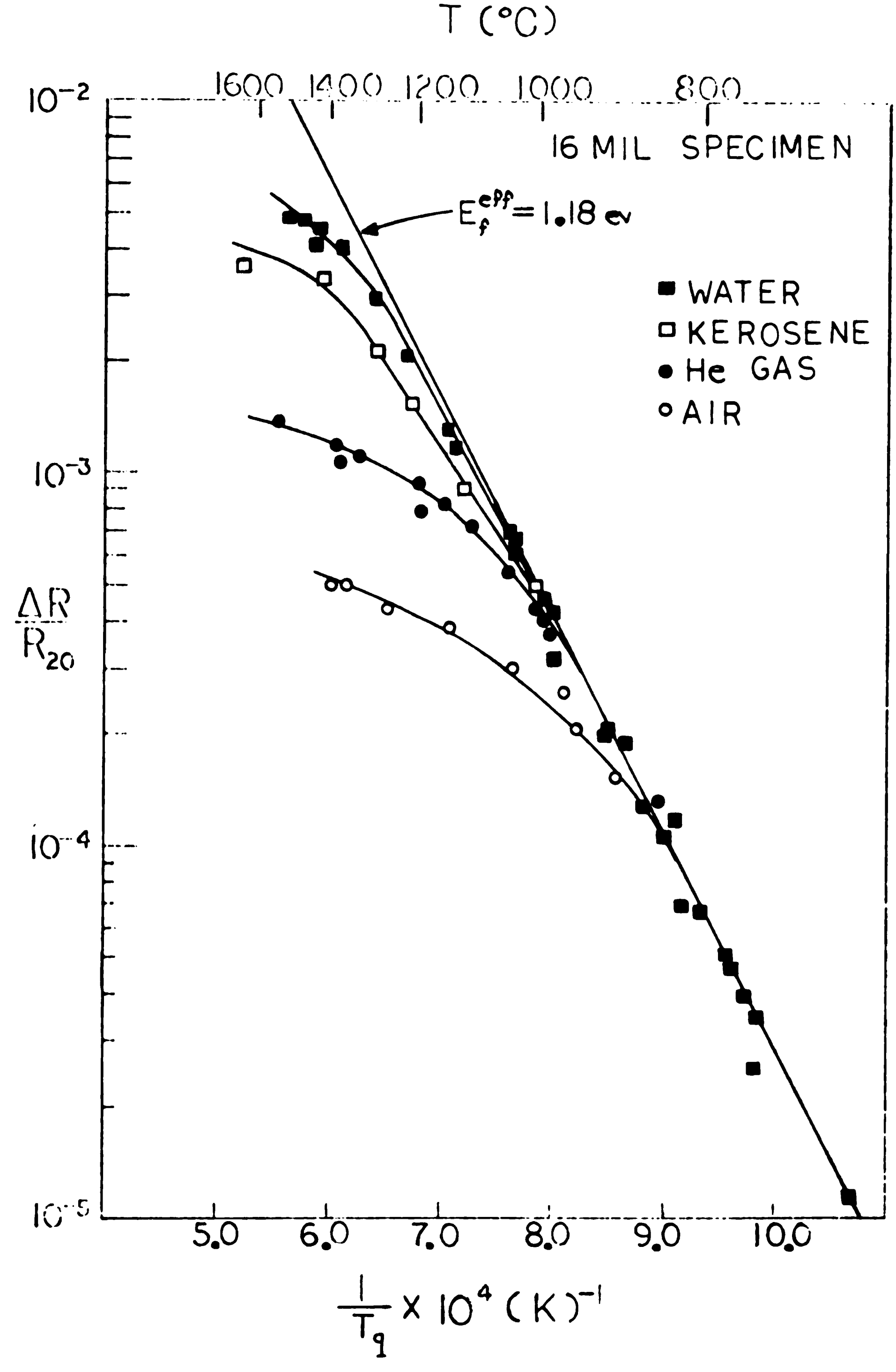

FIG. 17. — RESISTANCE QUENCHED INTO A 16 MIL SPECIMEN AS A FUNCTION OF QUENCH TEMPERATURE AND QUENCH SPEED.

quenches were done by abruptly shutting off the heating current and allowing the specimen to cool in the surrounding gas atmosphere.

2. Air and Slowed-Air Quenches-- 4 and 10 mil Wires

Air and slowed air quenches were performed on 4 and 10 mil specimens using the apparatus described in section III. In figure 18 we present data for a single 10 mil specimen obtained with direct air quenches and five slowed-air quench settings. Also included are water-quench data from the same specimen. In order to avoid the effects of liquid quenching strains on the air-quench data, the water quenches were done after nearly all the air and slowed-air quench data had been taken. Similar data, supplemented with flowing-air quenches, were obtained with two other 10 mil specimens and are shown in figure 19. Air and slowed-air quench data for a 4 mil specimen are presented in figure 20. The data obtained from direct air quenches with the 4 mil specimen yield an effective formation energy of E_f^{eff} = 1.30 ± 0.05 eV.

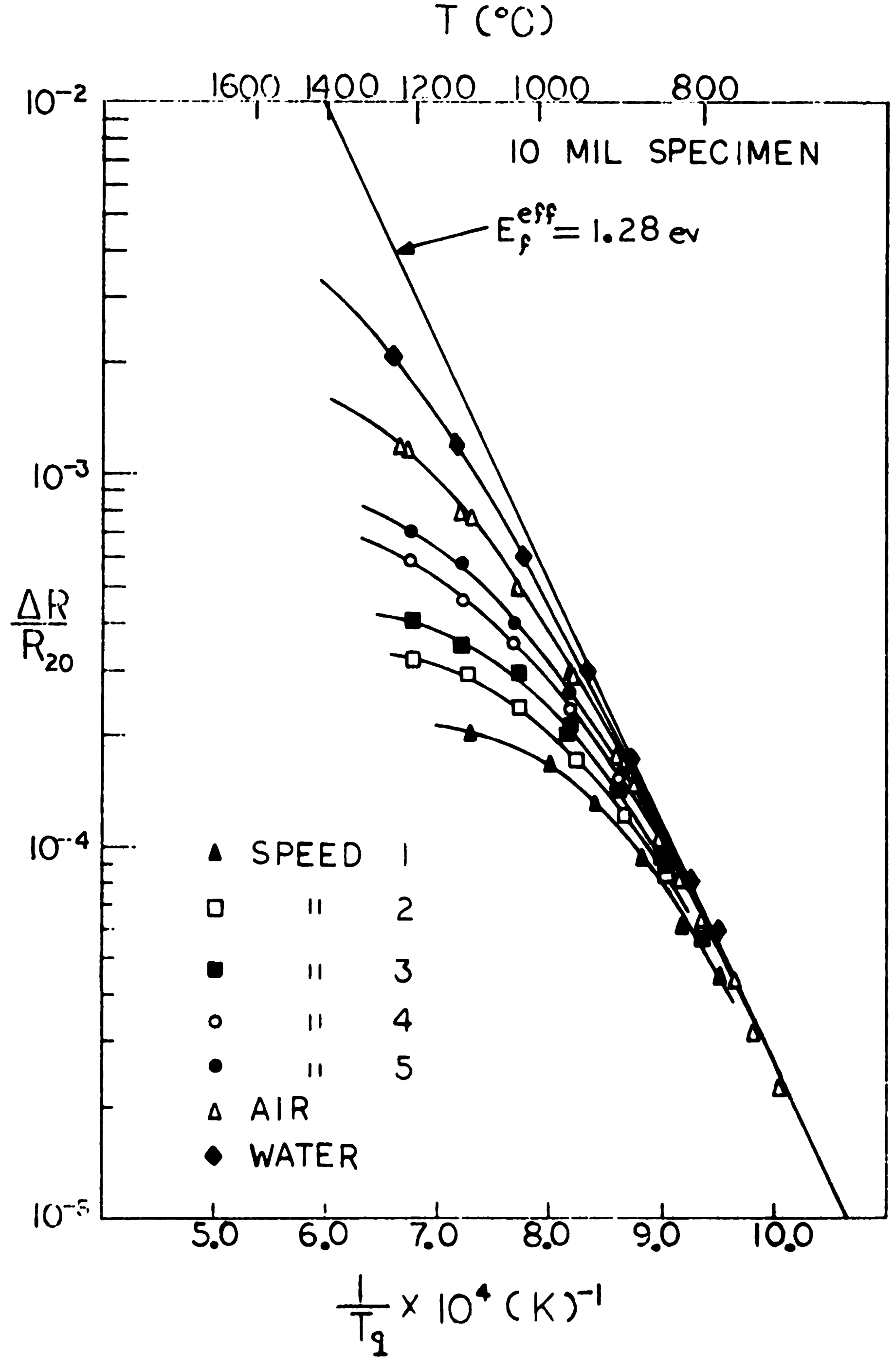

FIG. 18. — RESISTANCE QUENCHED INTO A 10 MIL SPECIMEN USING WATER, AIR, AND FIVE SLOW AIR QUENCH SPEEDS.

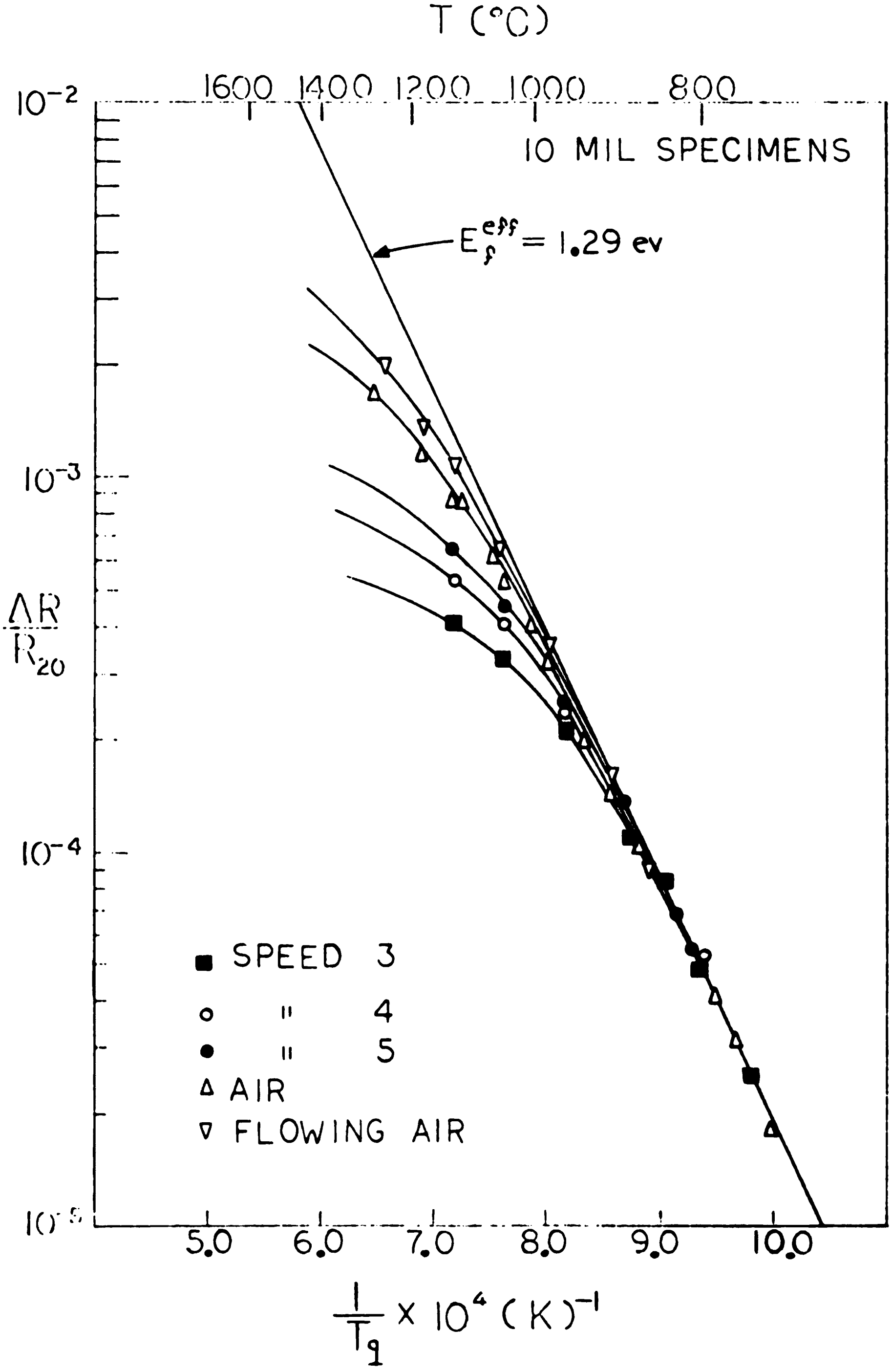

FIG. 19. — RESISTANCE QUENCHED INTO TWO 10 MIL SPECIMENS USING AIR, FLOWING AIR, AND 3 SLOW AIR QUENCH SPEEDS.

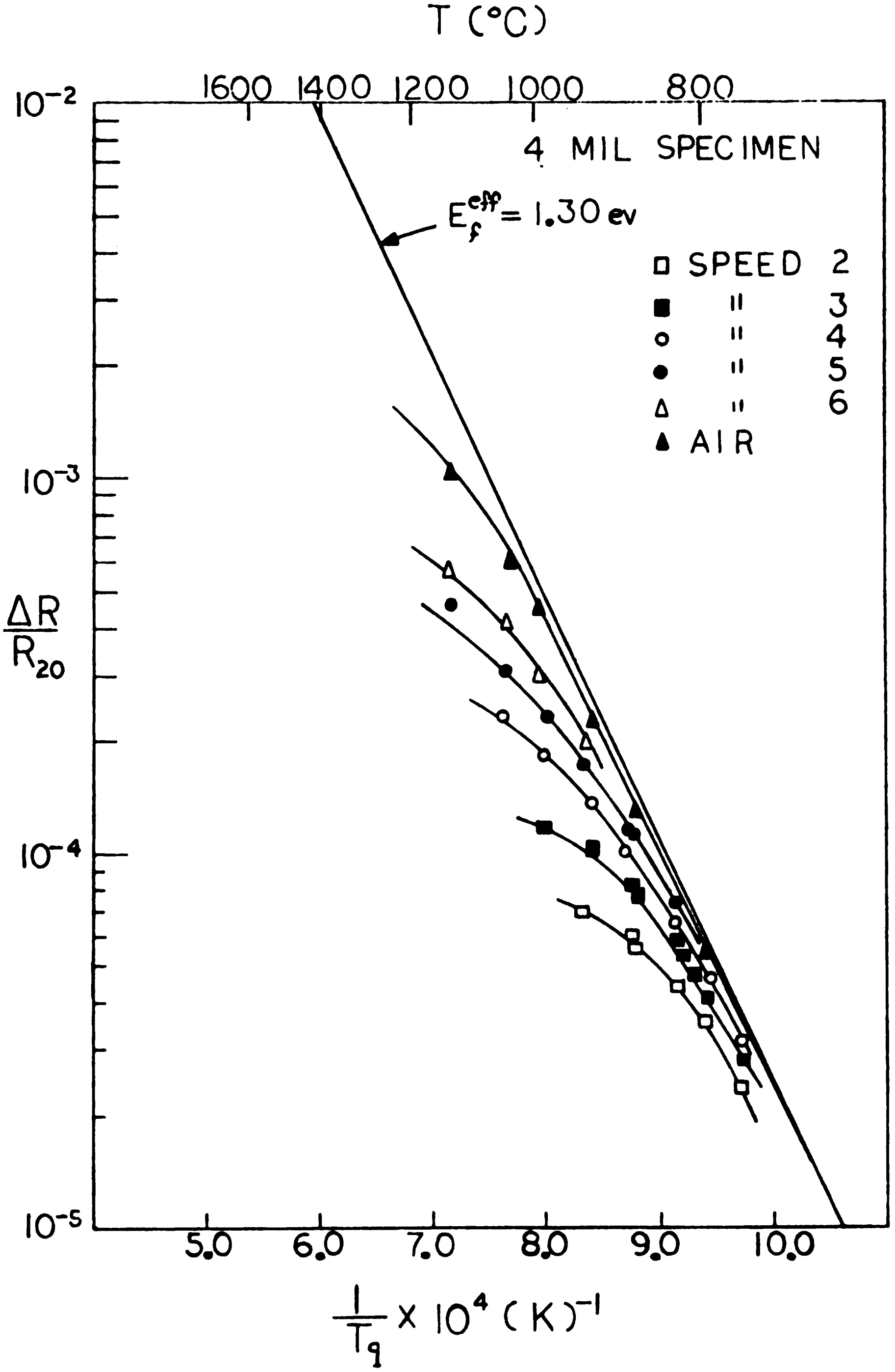

FIG. 20. — RESISTANCE QUENCHED INTO A 4 MIL SPECIMEN USING AIR AND 5 SLOW AIR QUENCH SPEEDS.

The major limitations on the accuracy of the quench data presented above are: 1) the same sources of uncertainty discussed in detail in section IV-C (which will not be discussed further here), and 2) variations in the quench speeds.

Variations in the water quench speeds were usually no larger than about 20% for a given specimen, and variations in the quench speeds for all gas and kerosene quenches were about 10% or less. The resultant variations in the quenched-in resistance produced by these variations in quench speed will increase systematically with increasing quench temperature. As is shown in section VI, a variation of 10% in the quench time will produce variations of 1, 4, and 10% in the quenched-in resistance for fractional vacancy losses in the vicinity of 10, 50, and 90%, respectively. For a 20% variation in the quench speed, the corresponding variations in the quenched-in resistance are 2, 10, and 25% respectively.

VI. ANALYSIS AND CONCLUSIONS

In sections IV and V, we showed that despite repeated efforts we could not reproduce Jackson's value of 1.51 eV for the vacancy formation energy in platinum. On the contrary, we obtained values of E_f^{eff} ranging from 1.2 eV for 16 mil diam wires to 1.3 eV for 4 mil diam wires. Because of both the disagreement between our data and Jackson's and the lack of internal consistency in our own data, we cannot follow through unambiguously with the original intent of the thesis--to test the Flynn et al. theory in a metal in which the value of E_f was reasonably well established. In such a case, we cannot pursue a test of the validity of the theory *per se*; or, in turn, use the theory to demonstrate the validity of either our data or Jackson's. However, we can still determine whether our complete data are consistent with the theory of Flynn et al., and if they are, whether the formation energy obtained is closer to our values or to Jackson's.

In the following, then, we apply the three tests for consistency with the Flynn et al. theory as discussed in section I.

A. The First Test

We first test whether the data of figures 17 to 20 are consistent with eqn 7. To do this, we assume values for E_f which then specify lines passing through the low temperature fast-quench data points. Each such line determines a series of quench temperatures T_q at which a given fraction of vacancies is lost during the quench, one for each quench time τ_q. According to eqn 7, a plot of $\ln(1/T_q\tau_q)$ versus $(1/T_q)$ should yield a straight line with slope $-E_m/k$. Figures 21, 22, and 23 contain such plots for the data of figures 17, 18, and 20, using values for T_q at which 50% of the assumed vacancy concentration was lost during the quench. Similar analyses using percent losses other than 50% showed no systematic differences from the results shown in figures 17, 18, and 20. Within the indicated uncertainties, the data are in

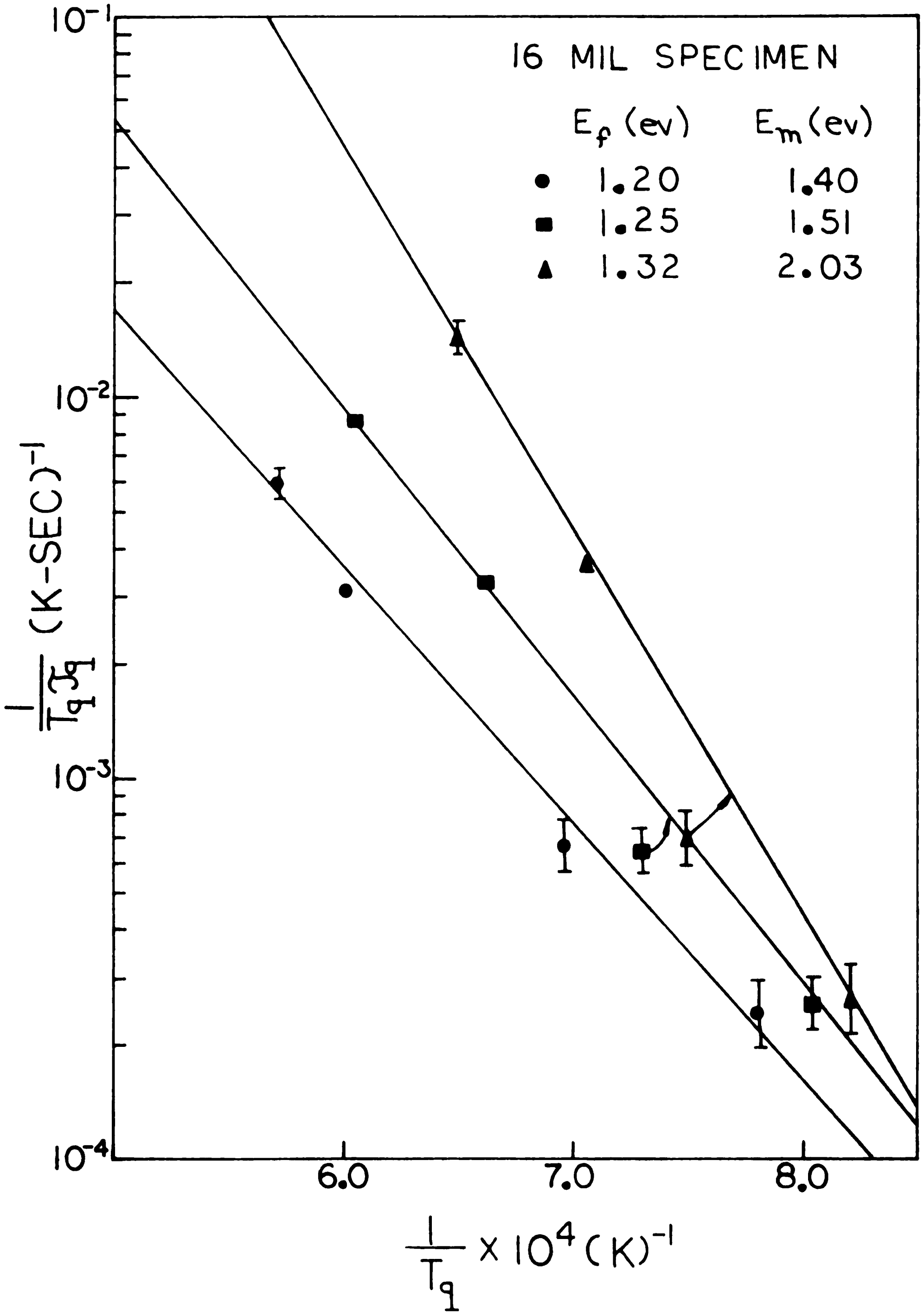

FIG. 21. — DETERMINATION OF E_M FOR ASSUMED VALUES OF E_F FOR A 16 MIL SPECIMEN USING THE FLYNN ET AL. ANALYSIS.

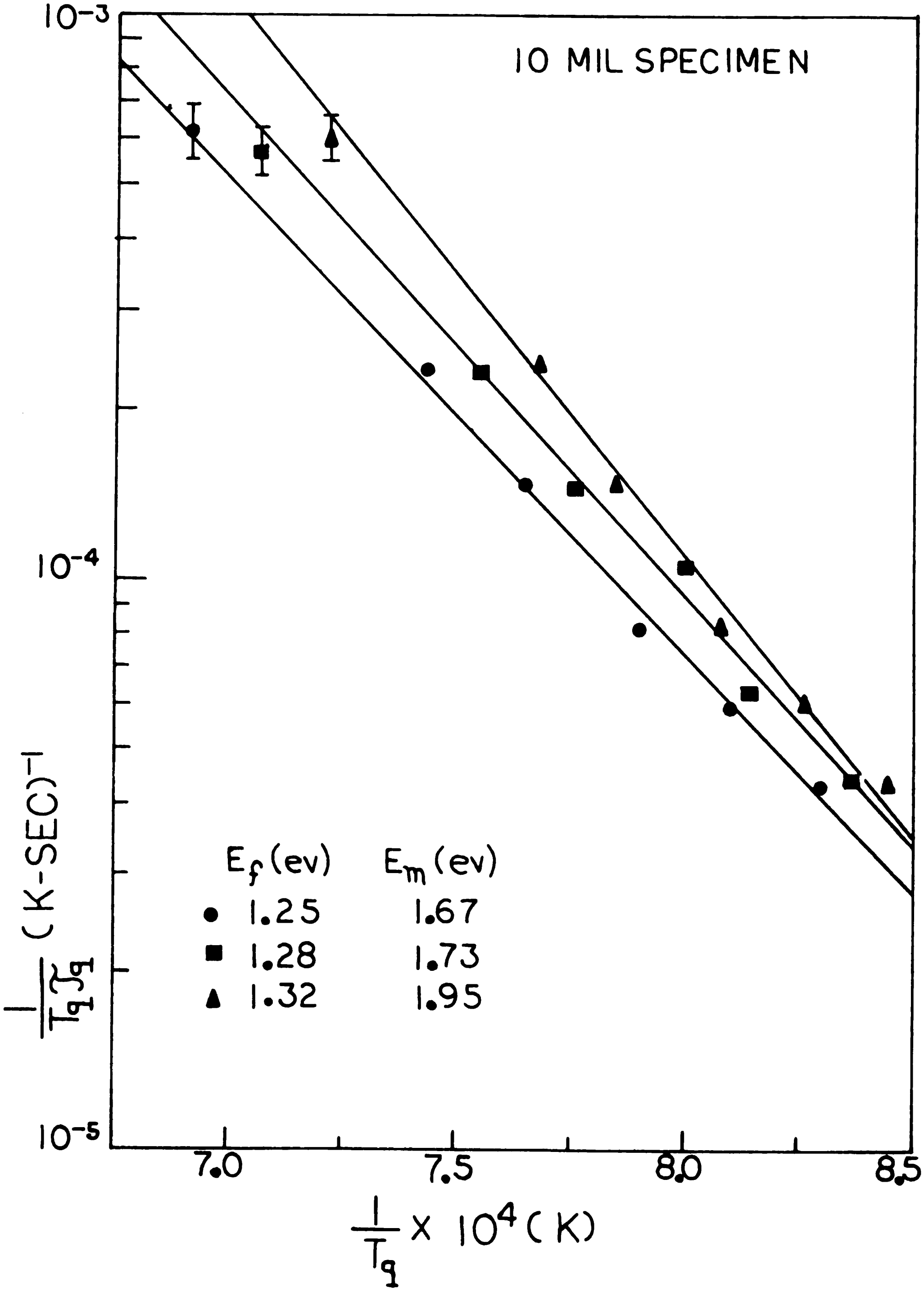

FIG. 22. — DETERMINATION OF E_M FOR ASSUMED VALUES OF E_F FOR A 10 MIL SPECIMEN.

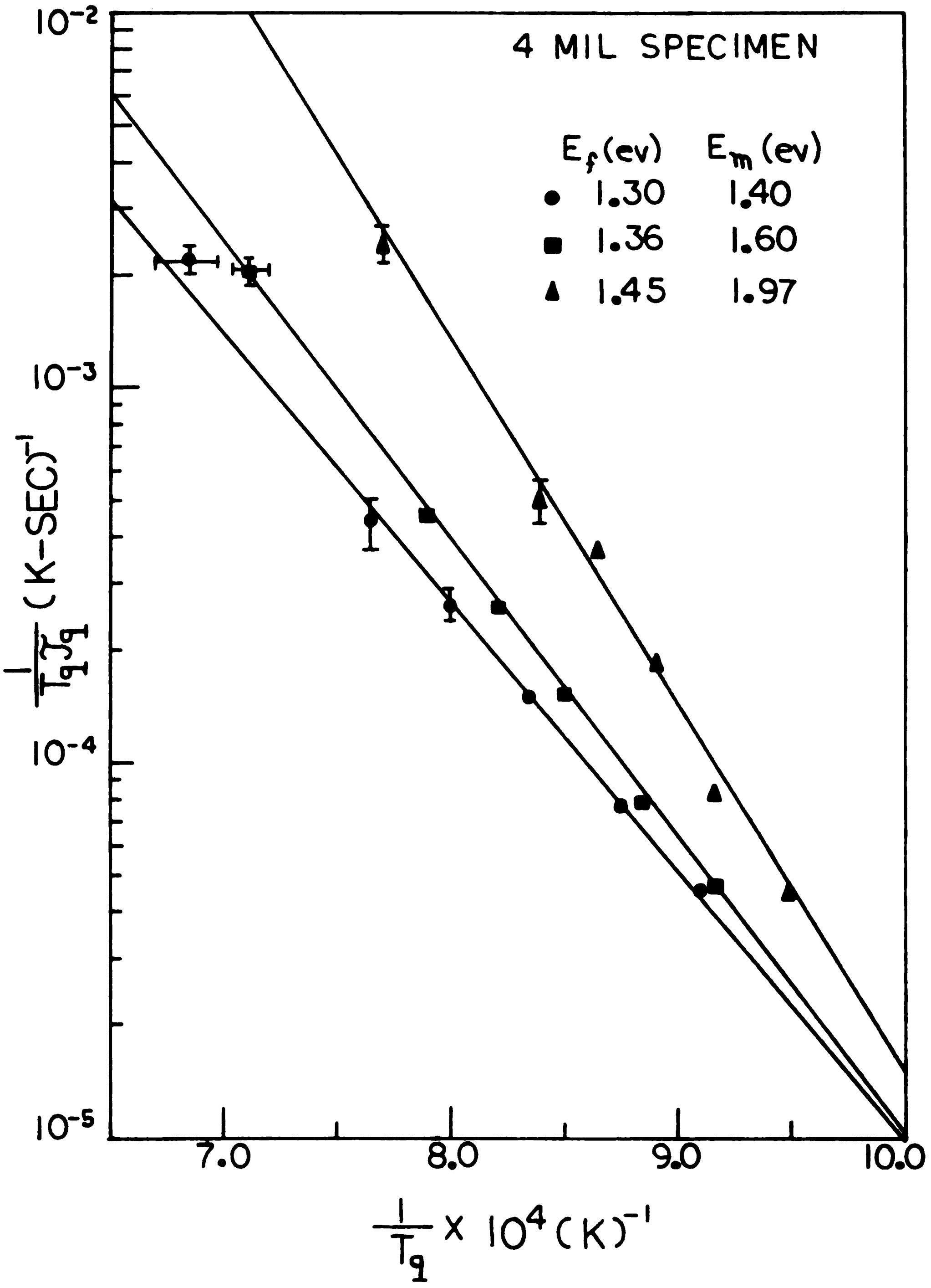

FIG. 23. — DETERMINATION OF E_M FOR ASSUMED VALUES OF E_F FOR A 4 MIL SPECIMEN.

general consistent with straight lines, for all three wire diameters, for wide ranges of T_q and τ_q, and for data obtained with both liquid and gas quenches.

The most significant deviations occur for the second lowest points with the 16 mil specimen (quenches in helium gas) and water quenches with the 10 mil specimen (not included in the data of figure 22). In the first case, we believe these deviations to be associated with an error in the determination of the effective quench temperature of the specimen, evidenced by the intermittant flashing of the specimen in the helium gas prior to quenching. Such errors in the quench temperature are much greater than any others incurred in all other liquid or gas quenches discussed in section IV. In the second case, the R-ratio of the 10 mil specimen in question was observed to fall by 10% after water quenching from its value after all air quenches had been completed. We believe this drop in the R-ratio to be caused by an increase in the specimen's sink density. Such a conjecture is consistent with the systematic shift of the water quench points in figure 26.

The error bars associated with certain points in each figure correspond to our estimate of the maximum uncertainty in τ_q or T_q. For quenches characterized to a good approximation by linear cooling curves (water, kerosene, and slowed-air quenches) the τ's were determined from $T_q/\dot{T}$, where T_q is the Kelvin quench temperature, and $\dot{T}$ is the linear quench speed obtained from the initial part of the temperature-corrected cooling curve. For direct air, flowing air, and helium gas quenches, the temperature-corrected cooling curves were first fit to the form $T(t) = T_q(1 + t/\tau_i)$, where the value of τ_i was determined by requiring that it give the best fit to the initial part of the actual cooling curve. The value of τ_i, so obtained, was increased by 25% to obtain the equivalent linear quench time τ_q. This latter procedure assumes the validity of the Flynn et al. theory, but should be as reliable as, and more internally consistent than, merely estimating an equivalent linear quench time by eye.

B. The Second Test

We next test to see whether the values of E_f and E_m paired by the above analysis give $Q = E_f + E_m = 2.90$ eV for assumed values of E_f of either 1.24 eV (our best value for E_f^{eff}) or 1.5 eV (Jackson's value). To do this, we plot in figure 24 the values of E_m deduced from the above analysis as a function of the assumed E_f. Included in this plot are data from analysis of an additional 10 mil specimen and of the same 16 mil specimen as in figure 17, with the data replotted to correct for a possible "temperature shift," as discussed in section IV. On the same graph we have drawn in the line $E_f + E_m = Q = 2.90$ eV. From this plot, we see that the 16 and 10 mil data fall in a band of width 0.05 eV, while the 4 mil data is shifted to the right by about 0.10 eV. From the intersection of this data with the 2.90 eV line, we obtain the following "best values" for E_f and E_m, consistent with $Q = 2.90$ eV:

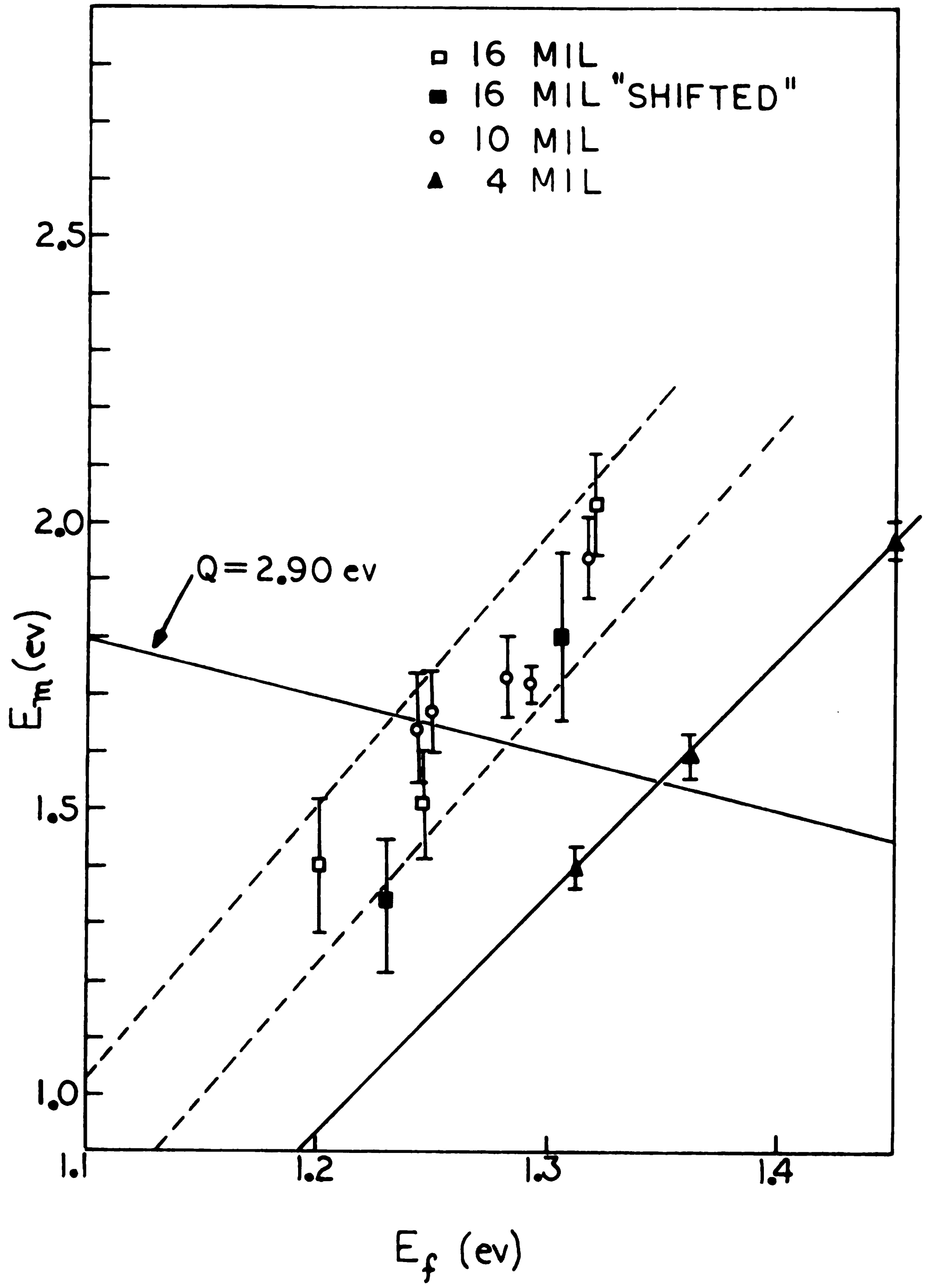

FIG. 24. — VALUES OF E_M DEDUCED FROM FLYNN ET AL. ANALYSIS VERSUS ASSUMED VALUES OF E_F FOR ALL THREE SPECIMEN DIAMETERS.

TABLE III

BEST VALUES OF E_f AND E_m DEDUCED FROM FLYNN ET AL. ANALYSIS FOR $Q = 2.90$ eV

16 and 10 mil specimens	$E_f = 1.25$ eV	$E_m = 1.65$ eV
4 mil specimen	$E_f = 1.35$ eV	$E_m = 1.55$ eV

Secondly, we see that for values of E_f greater than 1.45 eV the theory yields values for E_m of greater than 2.0 eV--values which are clearly unacceptable. Thirdly, we see that even though the theory does yield pairs of values for E_f and E_m which are consistent with Q when our own values for E_f are used with it, these values are not the same for all specimens. Thus according to this second test, we can only say that for each specimen diameter the data are consistent with the theory.

C. The Third Test

The third test for consistency of our data with the theory of Flynn *et al.* is whether the data exhibit a fractional vacancy loss during the quench which depends only on the product $D_q T_q \tau_q$. Thus, when the quench data for various T_q and τ_q are plotted together, a single curve should result: that is

$$c/c_o = f(D_q T_q \tau_q), \qquad [8a]$$

where c/c_o is the fractional concentration of vacancies remaining after a quench from temperature T_q with quench time τ_q. Since the values of $D_q T_q \tau_q$ commonly run over 3 or more orders of magnitude, it is useful to plot

$$c/c_o = f'[\ln(D_q T_q \tau_q)] \qquad [8b]$$

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

Such plots are shown in figures 25, 26, and 27 for the quench data of figures 17, 18, and 20. For explicitness, the values chosen for E_f and E_m are those obtained from the analysis in part B for Q = 2.90 eV. In each case, the data are observed, in general, to lie on a single curve, in agreement with the predictions of the

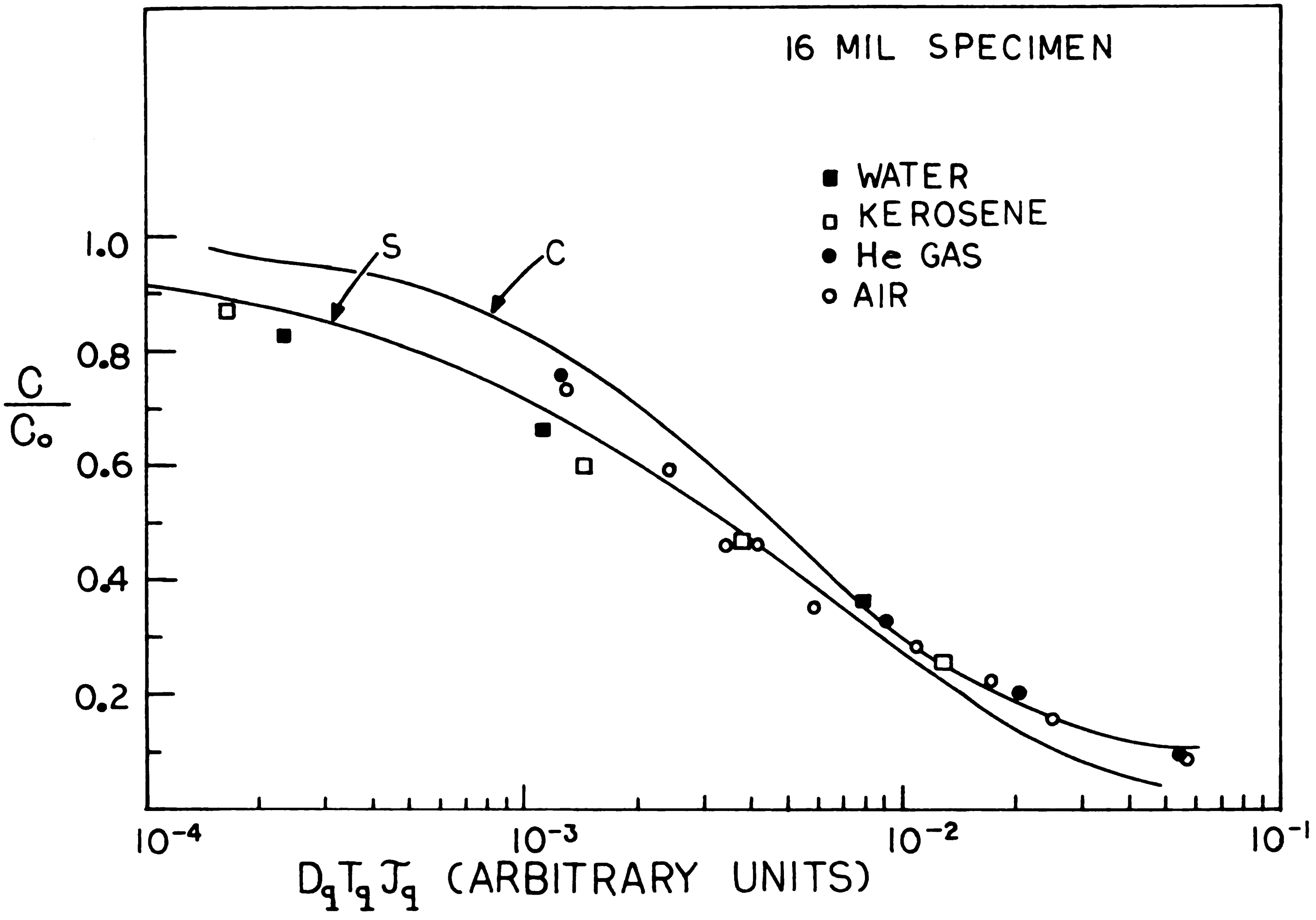

FIG. 25. — FRACTIONAL QUENCHED-IN VACANCY CONCENTRATION C/C_0 VERSUS $D_Q T_Q \tau_Q$ FOR A 16 MIL SPECIMEN USING $E_F = 1.25$ eV, $E_M + E_M = 1.65$ eV, AND $Q = 2.90$ eV.

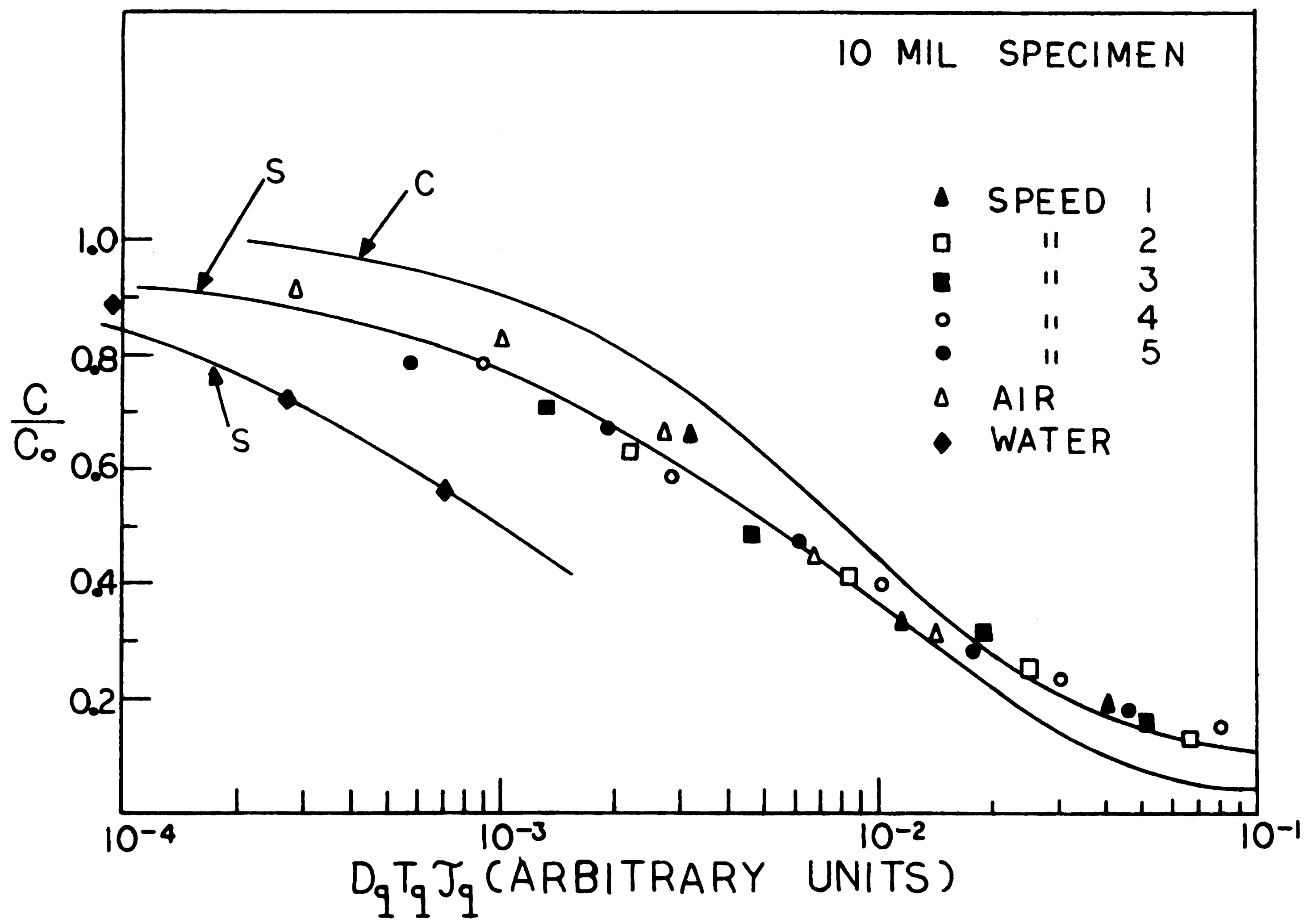

FIG. 26. — FRACTIONAL QUENCHED-IN VACANCY CONCENTRATION $C/_{C_0}$ VERSUS $D_Q T_Q \tau_Q$ FOR A 10 MIL SPECIMEN USING $E_F = 1.25$ eV, $E_M = 1.65$ eV AND $Q = 2.90$ eV.

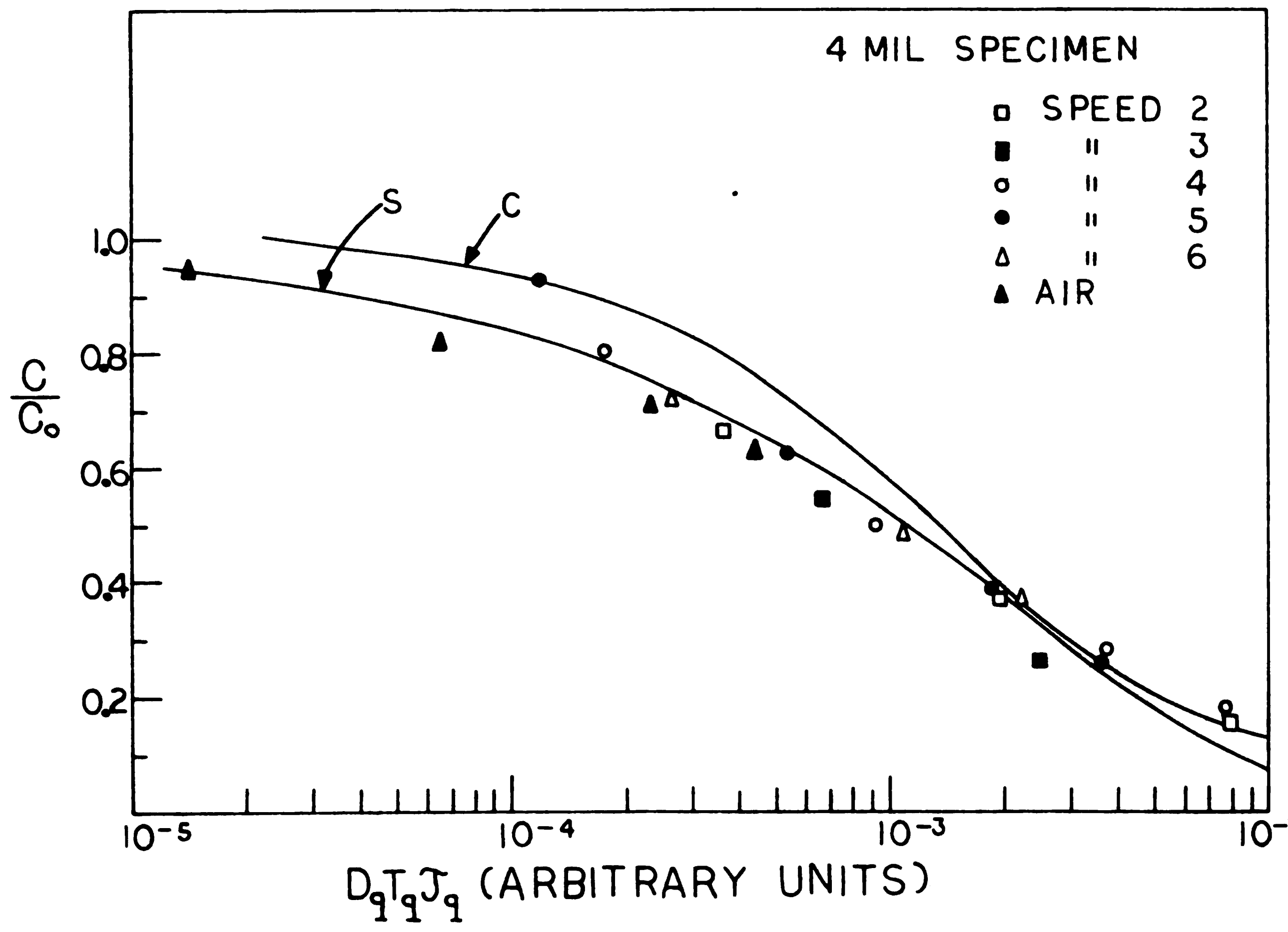

FIG. 27. — FRACTIONAL QUENCHED-IN VACANCY CONCENTRATION C/C_O VERSUS $D_Q T_Q \tau_Q$ FOR A 4 MIL SPECIMEN USING $E_F = 1.35$, $E^M = 1.55$ eV AND $Q = 2/90$ eV. CURVES LABELED C AND S CORRESPOND TO FLYNN ET AL. THEORETICAL CURVES FOR VACANCY LOSS TO CYLINDRICAL AND SPHERICAL SINKS, RESPECTIVELY.

Flynn et al. theory. In figure 25 the data from figure 17 have first been corrected for a possible "temperature shift" as discussed in section IV. The uncorrected data fit well to spherical sinks only for $E_f = 1.18$ eV. The shift of the 10 mil water quench points has been discussed above and is consistent with an increase in the specimen sink density.

In addition to showing that the vacancy loss is a function of $D_q T_q \tau_q$ only, one can now attempt to see whether the function f' corresponds to either of those predicted by the Flynn et al. theory for a specific geometric sink structure. That is, if the dominant sinks in the specimen are uniformly spaced dislocations, approximated as the core of a cylinder, the predicted vacancy-loss curve will be given by the curve labeled C in figures 25, 26, and 27. However, if the dominant sinks are uniformly spaced grain boundaries, approximated as the surface of a sphere, the predicted vacancy-loss curve will be given by the curve labeled S in figures 25, 26, and 27. As is seen in these three figures, the data are approximated quite well by the curve for spherical sinks for the values of E_f and E_m obtained for the analysis in part B. Further, for no reasonable choices of E_f or E_m are the data approximated well by the curve for cylindrical sinks. Once again, we see that for each specimen diameter the data are consistent with the predictions of the theory. Also, when one attempts to fit the vacancy-loss data with values of E_f as high as 1.50 eV, the resulting curves are extremely flat and resemble neither the curves for cylindrical or spherical sinks.

D. Summary and Discussion

Having obtained estimates for E_f and E_m in the preceding sections, we note that the value of E_f so obtained is not in agreement with that obtained by Jackson, nor is the value of E_m so obtained in agreement with that commonly found from low-temperature annealing studies (see Table I). We will now analyze our results for internal consistency and for possible explanations for their lack of agreement with those of other studies. We begin with a summary of our estimates for E_f by two different methods.

1. Determination of E_f from Fast, Low-temperature Quenches

From low-temperature water quenches of 16 and 10 mil specimens, and direct air quenches of 4 mil specimens, we obtained the following results:

TABLE IV

VALUES OF E_f^{eff} OBTAINED FROM FAST-QUENCH DATA FOR ALL THREE SPECIMEN DIAMETERS

Specimen diameter (mil)	E_f^{eff} (eV)
16	1.20 ± .04
10	1.26 ± .04
4	1.30 ± .05

Since in part I of the results, we have discussed extensively our water-quench data *vis a vis* Jackson's results, we shall not go into further discussion of it here.

2. Determination of E_f from Flynn et al. Analysis

In parts A, B, C, of the Analysis we applied the Flynn et al. analysis to the raw data given in part II of the results, and found that for any given specimen diameter the data passed all tests for consistency with the theory. For Q = 2.90 eV (the value obtained from self-diffusion experiments), the analysis selected a pair of values (E_f, E_m) consistent with the requirement $E_f + E_m = Q$. These results are presented in Table III. By comparison of Tables III and IV, we see that the values of E_f determined by method 2) are in satisfactory agreement--for each specimen diameter--with those obtained from method 1). However, all of these values are considerably smaller than the value of 1.51 eV obtained by Jackson (33). Faced with such an obvious disagreement, we will examine the two possibilities: 1) Jackson's results are wrong, or 2) our results are wrong.

Let us first consider the possibility of error in Jackson's results. First, we note that there does not yet exist adequate independent confirmation of Jackson's value for E_f. The only subsequent quenching study obtained the value $E_f = 1.46 \pm 0.02$ eV. However, this value was obtained using only three data points, and we believe that its uncertainty is likely to be considerably greater than quoted. In any case, the value is as consistent with $E_f = 1.40$ eV as it is with 1.51 eV, and therefore represents at best only modest support for Jackson's result. Second, the fact that Jackson's values for E_f and E_m add up to Q is not adequate proof that his results are correct. Misek's quite different results also satisfied this criterion. Third, Jackson's value for E_m was obtained from low temperature annealing studies, which are known to be subject to substantial errors associated with vacancy-vacancy and vacancy-impurity interactions (4, 11). The difficulties involved are adequately illustrated by the range of values for E_m quoted in Table I, when it is realized that some investigators found these values to vary with quench temperature and some did not. Thus, it is not difficult to conceive of future experiments using still lower quenching temperatures and still more pure specimens producing values for E_f^{eff} 0.1

or 0.2 eV higher than those now available. Finally, although Jackson clearly performed a comprehensive and careful study of quenched platinum, the possibility of a systematic error cannot be completely precluded.

We now consider the possibility of error in our own results. In section IV we analyzed our data for a series of random and systematic errors, and concluded that these were not large enough to reconcile the differences between our low temperature fast-quench data and Jackson's. At the same time, we observed that none of the "systematic errors" proposed by Jackson to dispose of earlier data appeared to be present in our low temperature fast-quench data. In Appendix A we discuss a difficulty in the study of quenched platinum which might have affected both our data and Jackson's, and whose effects are not yet clear. We now consider those effects which have not yet been discussed in detail which might possibly have produced the necessary systematic errors in our data. There are three such effects: 1) vacancy-vacancy clustering into small mobile defects (Perry's objection (24) to the Flynn et al. extrapolation procedure); 2) quenching strain (Seeger and Mehrer's objection (4) to the extrapolation procedure); and 3) the possibility that the vacancies anneal to other than fixed sinks (e.g. to nucleii established during the quench).

1) Vacancy-vacancy clustering: If vacancies cluster together during the quench to form small highly mobile di-vacancies, then we would expect to find greater vacancy loss under conditions where more di-vacancies form. Fast quenches from low temperatures should show the smallest effect of such clustering. Slow quenches, particularly those from high temperatures, should show the largest effect. Thus we would expect our low temperature fast quench data to be little changed, and our high temperature slow quench data to be reduced in magnitude from what it would have been in the absence of cluster formation. Examination of the data of figure 20 shows that this would lead to lower values for E_m for a chosen value of E_f, and thus to higher estimates for the value of E_f necessary to satisfy the condition $E_f + E_m = Q$. This is just the opposite of what we find. Our values for E_f are considerably smaller than Jackson's value.

2) Seeger and Mehrer (4) suggested that in gold quenching strains might be the source of an incorrectly high value for E_f obtained from the Flynn et al. extrapolation. This is also the opposite of what we find in platinum. Thus, if we are to understand the difference between our results and Jackson's in terms of quenching strain, we cannot use Seeger and Mehrer's arguments. Rather, we must use Jackson's argument that quenching strain is largest for quenches from higher temperatures, and in this case leads to less vacancy retention, because of an increase in sink density produced by the strain. Qualitatively, this mechanism describes what happened, since greater vacancy loss at high temperatures would produce smaller estimates for E_f (see argument in section 1 just above). While we cannot completely rule out this possibility, our tests for quenching strain strongly suggest that they are too small to explain the total difference between our values for E_f and Jackson's.

3) Annealing to other than fixed sinks: We note first that just as in previous studies of gold (3), aluminum (20), and tungsten (23), our data are consistent

in form with what would be expected for annealing of single vacancies to uniformly spaced spherical sinks, such as grain boundaries. However, this is not a proof that such annealing is actually occurring. A better argument comes from the available electron microscope studies of quenched platinum (43, 44), in which it was found that only few, small clusters formed in quenched platinum.

We conclude that while the possibility for systematic error in our experimental data exists, we cannot identify either a single source or combination of sources which obviously explain the difference between our values for E_f and Jackson's.

E. Conclusion

The differences between our values for E_f and Jackson's are real, and difficult to understand. We cannot say for sure which of us is correct. We would like to see one more, careful study of quenched 16 mil dram wires using low temperature fast quenches, in order to see whether our data or Jackson's is reproduced.

Otherwise we see no advantage in further quenching studies of platinum using only measurements of electrical resistance. We badly need either quenching studies combined with direct observation of vacancies using the Field-ion-microscope, or the application of the Simmons-Balluffi technique to platinum.

We are bothered by the failure of the data obtained with different specimen sizes to be the same. The explanation may lie in the effects of impurities, of quenching strain, or vacancy-vacancy clustering. In any case, this disagreement means that the Flynn, Bass, and Lazarus theory must be applied with care, and that it must be tested upon samples having substantially different diameters if extremely accurate results are to be obtained. Only if there is agreement for data taken on different wire sizes can the data be accepted as accurate.

To see whether one final explanation could be the answer to our problems, we used Takamura's suggestion (49), and extrapolated our data to "infinitely thin" sample diameter. The resulting E_f lay between 1.30 and 1.35 eV, on the upper end of the results previously obtained, and still in disagreement with Jackson's results.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. L. A. Girifulco, Atomic Migration in Crystals, Blaisdell Publishing Co., New York (1964).

2. R. O. Simmons and R. W. Balluffi, Phys. Rev., **117**, 52 (1960).

3. C. P. Flynn, J. Bass and D. Lazarus, Phil. Mag., **11**, 521 (1965).

4. A. Seeger and H. Mehrer, Vacancies and Interstitials in Metals, North Holland Publ. Co., Amsterdam (1970) p. 1.

5. R. O. Simmons and R. W. Balluffi, Phys. Rev., **119**, 600 (1960).

6. R. Feder and A. S. Nowick, Phil. Mag., 15, **805** (1967).

7. G. A. Sullivan and J. W. Weymouth, Phys. Rev., **9**, 89 (1964).

8. R. O. Simmons and R. W. Balluffi, Phys. Rev., **125**, 862 (1962).

9. V. G. Weizer and L. A. Girafalco, Phys. Rev., **89**, 848 (1968).

10. M. de Jong and J. S. Koehler, Phys. Rev., **129**, 40 (1963).

11. K. P. Chik, Vacancies and Interstitials in Metals, North Holland Publ. Co., Amsterdam (1970), p. 183.

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

13. C. J. Meechan and J. A. Brinkman, Phys. Rev., 103, 1193 (1956).

14. P. Simson and R. Sizmann, Z. Naturf., 174, 596 (1962).

15. J. Mori, M. Meshii, and J. W. Kauffman, J. Appl. Phys., 33, 1671 (1962).

16. J. Bass, Thesis, Univ. of Illinois (1964).

17. T. Kino and J. S. Koehler, Phys. Rev., 162, 632 (1967).

18. R. W. Balluffi, R. W. Siegel, K. H. Lie and D. N. Siedman, Vacancies and Interstitials in Metals, North Holland Publ. Co., Amsterdam (1970), p. 125.

19. C. B. Wang, D. N. Seidman and R. W. Balluffi, Phys. Rev., 169, 553 (1968).

20. A. Seeger and H. Mehrer, Phys. Stat. Sol., 29, 231 (1968).

21. J. Bass, Phil. Mag., 15, 136 (1967).

22. N. L. Peterson and S. J. Rothman, Phys. Rev., 1, 3264 (1970).

23. R. J. Gripshover, M. Khoshnevisan, J. Zetts, and J. Bass, Phil Mag., 22, 178 (1970).

24. A. J. Perry, Phil. Mag., 21, 743 (1970).

25. B. G. Lazarev and O. N. Ovcharenko, Dokl. Akad. Nauk., S.S.R., 100, 5 (1955).

26. F. J. Bradshaw and S. Pearson, Phil. Mag., 1, 812 (1956).

27. A. Ascoli, M. Asdente, E. Germagnoli, and A. Manara, J. Phys. Chem. Solids, 6, 59 (1958).

28. G. L. Bacchella, E. Germagnoli, and S. Granata, J. Appl. Phys., 30, 748 (1959).

29. G. R. Piercy, Phil. Mag., 5, 201 (1960).

30. K. Misek, Phys and Tech. of Low Temps. Publ. House Czech. Acad. Sci., Prague, 1964, p. 110.

31. V. S. Kopan, Fiz. Metal. Metallovod, 19, 569 (1965).

32. J. J. Jackson, Lattice Defects in Quenched Metals, Academic Press, New York (1965), p. 467.

33. J. Baumgarten, F. Heigl and R. Sizmann, KFA Report, International Conf. on Vacancies and Interstials in Metals, Jülich, 1968, vol. 1, p. 124.

34. J. Polák, Phys. Stat. Sol., 28, 773 (1968).

35. D. Schumacher, A. Seeger and O. Harlin, Phys. Stat. Sol., 25, 359 (1968).

36. R. Rattke, O. Hauser and J. Wieting, Phys. Stat. Sol., 31, 167 (1969).

37. S. D. Gerstriken, and N. N. Novikov, Phys. Metals Mettalog. (USSR) (English Trans.), 11, 78 (1961).

38. Ya. A. Kraftmakher, and E. B. Lanina, Sov. Phys. Sol. State, 7, 92 (1965).

39. C. V. Kidson, and R. Ross, Proc. Intern. Conf. Radioisotopes Sci. Res., Paris, 1, 185 (1957).

40. F. Cattaneo, E. Germagnoli, and F. Grasso, Phil. Mag., 1, 1373 (1962).

41. M. Hoch, Vacancies and Interstials in Metals, North Holland Publ. Co., Amsterdam (1970), p. 81.

42. E. Ruedl, P. Delavignette, and S. Amelinckx, *Radiation Damage in Solids*, Vol. I, p. 363, International Atomic Energy Agency, Vienna, 1962.

43. R. W. Newman, Thesis, Univ. of Florida (1967).

44. D. Seidman--Personal Communication.

45. *Temperature, Its Measurement and Control in Science and Industry*, Reinhold Publ. Co., New York (1941), p. 1312.

46. R. J. Gripshover, Thesis, Mich. St. Univ. (1969).

47. J. J. Jackson, Personal Communication.

48. J. J. Jackson, *Lattice Defects in Quenched Metals*, Academic Press, New York (1965), p. 479.

49. J. Takamura, *Lattice Defects in Quenched Metals*, Academic Press, New York (1965), p. 521.

50. A. B. Lidiard, Phil. Mag., **5**, 1171 (1960).

51. R. H. Freeman, F. J. Blatt, and J. Bass, Phys. Kondens. Materie, 271, 282 (1969).

52. M. Doyama, Phys. Rev., **148**, 681 (1966).

53. K. P. Cizek, Czech, J. Phys., **1317**, 186 (1967).

54. R. Gripshover, J. Zetts, and J. Bass, KFA Report, International Conf. on Vacancies and Interstitials in Metals, Jülich, 1968, Vol. I, p. 228.

55. K. Misek, Czech. J. Phys., **1317**, 647 (1967).

56. J. Bass, Phys. Rev., **137**, A765 (1965).

57. R. M. Emrick, Phys. Rev., **122**, 1720 (1961).

58. R. R. Conte and J. Dural, Phys. Lett., 27A, 368 (1968).

59. R. J. Berry and J. L. G. Lamarche, Phys. Lett., 31A, 319 (1970).

APPENDICES

APPENDIX A

DATA SHIFTS

In figures 10 and 12 we compared the resistance quenched into various 16 mil diameter wires and noted that all data obtained with specimens given the shorter, high temperature anneals are shifted to the right of those obtained with specimens given the longer anneals. Also, the further the data are shifted to the right, the lower, in general, is its slope. In addition to these inter-specimen data shifts, intra-specimen data shifts were observed in specimens of all three sizes. The shifts were found most often in specimens which had been quenched at least 25 times and, especially, from temperatures above 1200°C. In these cases, the new low-temperature data line was shifted to the right of the original line, and had an equal or slightly smaller slope. The shift was usually accompanied by a substantial drop in the specimen's resistance ratio (in one case by a factor of 3-1/2). The new high temperature data would gradually approach the original data and, occasionally, cross over it. In two cases, the new data were shifted by the equivalent of as much as 35K° from the old.

Since it is not necessarily true that both the inter- and intra-specimen data shifts are associated with a single phenomenon, we have considered in some detail two possible causes for each: 1) a shift in the specimen's resistance versus temperature curve from the N.B.S. curve (resulting primarily in a change in the effective quench temperature, but no change in the quenched-in resistance from the "true" quench temperature); and 2) a change in the specimen's impurity content or distribution, which produces at any temperature a change in quenched-in resistance from what would have been obtained with a "pure" specimen. (In this case we assume that the impurity content is not large enough to measurably affect the resistance versus temperature curve). Such a distinction between a temperature shift and the effects of impurities is somewhat artificial, since a temperature shift must necessarily be due to some physical change in the specimen.

However, as we shall see below, the distinction can be useful in analyzing the data.

A shift in a specimen's resistance-temperature curve would result in an error in the determination of the quench temperature. Equation 4 would only correctly describe the quench data if the data were explicitly corrected for this temperature shift (i.e., one had an independent means for measuring the temperature). If such a temperature shift exists, the data are described by the equation

$$\Delta R_Q = R_o \exp\left[-\frac{E_f}{K}\left(\frac{1}{T + \Delta(T)}\right)\right], \qquad (9)$$

where $\Delta(T)$ is the difference between T, the temperature determined from the specimen's resistance ratio, and the true temperature, $T + \Delta(T)$. For the simplest case, $\Delta(T)$ independent of T over the entire quench-temperature range, the logarithmic plot of ΔR_Q versus $\frac{1}{T}$ will be nearly linear and will for Δ positive (negative) have a smaller (larger) slope than that of equation 4 . The data will also be shifted from that of equation 4 , and, because $\frac{1}{T}$ is a non-linear function of T, the shift will be largest at the lowest temperatures. For $\Delta = +40°C$, and the same E_f^v, the slope given by equation 9, is about 7% (0.08 eV) lower than that given by equation 4 for $E_f = 1.23$ eV.

The presence of impurities could affect the quench data in a number of ways, depending upon the type of impurities involved and their concentration. For an impurity concentration much larger than the concentration of vacancies in the pure metal (C_v approximately 10^{-4}), an excess number of vacancies can be quenched into the specimen in the form of vacancy-impurity complexes. If no vacancies are lost during the quench, the excess resistance $R_V^I(T)$ quenched into the impure specimen is given by (50)

$$R_V^I(T) = R_V^P(T) \; [(1-12C_I) + C_I\delta \; e^{B/KT}], \qquad [10]$$

where $R_V^P(T)$ = vacancy resistance in the pure metal at temp. T.

B = vacancy-impurity binding energy

C_I = impurity concentration

δ = correction factor for the effective resistance of a vacancy-impurity pair.

For positive B, the logarithmic plot of the quenched-in resistance versus $\frac{1}{T}$ will be shifted to the right of the pure-specimen data, and will have a lower slope. The shift will again be largest at the lowest quench temperatures. In addition, for high quench temperatures and slow quenching rates, vacancy-impurity complexing might retard the migration of vacancies to sinks during the course of a quench, thus, producing a larger quenched-in resistance than would have occurred in the pure specimen. Finally, the impurities themselves might move in and out of solution during quenching and annealing, causing further perturbations in the quenched-in resistances.

Before proceeding further, it should be noted that, in the absence of reliable chemical or spectroscopic analysis of the specimens, the specimen's residual resistance ratio (R-ratio) is the only available measure of its impurity content. However, there are several problems involved in using the resistance ratio as a unique measure of specimen purity. For one, the base resistance in liquid helium, R_B, is also sensitive to the specimen's internal structure (grain and sub-grain size, dislocation density, etc.). Thus, it is difficult to determine whether changes in a specimen's resistance ratio, caused primarily by changes in R_B, are due to changes in its impurity content or internal structure. (Simple geometry changes should cause no change in the R-ratio.) A second, and possibly more fundamental problem, is whether greater impurity concentrations always produce lower resistance ratios and whether the same impurity content always produces the same ratio (e.g. for a given impurity concentration the ratio could change significantly depending upon whether the impurities were distributed uniformly throughout the lattice, collected at grain boundaries, or relegated to a few atomic layers at the specimen surface). Phenomena possibly associated with such problems were observed in 4 mil specimens and are discussed below.

Returning to the data of figure 12, we see that both equation 9 (a temperature shift) and equation 10 (the presence of impurities) have the qualitative form necessary to describe the observed data shifts. We now consider whether either equation can explain the magnitude of the shifts in detail. We begin with equation 9.

The initial purity of all specimens used was given as 99.999% by the supplier, Sigmund Cohn Inc. Subsequent spectroscopic analysis (51) performed by Cominco Inc. of 16, 10, and 2 mil platinum wires taken from the same rolls as several specimens used in this study yielded impurity concentrations in good agreement with the purity claimed by the supplier. The largest single contaminant common to all three wire sizes was silicon, whose concentration was about 1 part per million (ppm) in the 16 and 10 mil wires and 5 ppm in the 2 mil wires. (No 4 mil wires were submitted for analysis.) Thus it seems unlikely that impurity concentrations greater than a few ppm were initially present in the wires used in this study.

Now, returning to the data shifts of figure 12, we see that the highest data line F gives quenched-in resistances approximately two times larger than the lowest data line A for $\frac{1}{T} \simeq 10 \times 10^{-4}$ ($T_q = 1000°K$). Assuming that this increase in quenched-in resistance is caused by an impurity concentration of no larger than 10 ppm, equation 10 requires an associated binding energy of nearly 0.8 eV to describe the observed data.

Such a binding energy is significantly greater than those reported for any impurities in fcc metals (52). While larger impurity concentrations could be obtained if the specimens had been contaminated during the initial annealing and quenching, all but one of the specimens had R-ratios of 4000 to 5700 after the initial anneal and low-temperature quenches (see Table II). These resistance ratios are consistent with a total impurity concentration of less than 10 ppm. In addition, from the spectrographic analysis mentioned above, no significant difference in the impurity concentrations were observed when 16 or 10 mil wires were annealed at high or low temperatures, or not annealed at all. Finally, the positions and slope of the various data lines of figure 12 show no obvious systematic dependence upon R-ratio for the full range of ratios studied (800-5700). Thus it seems unlikely that the simple impurity effects associated with equation 10 are responsible for the shifts in the data.

It is worth noting that several previous experimenters have observed effects in quenched or annealed-platinum wires which appear to be associated with impurities. Jackson (32) quenched 16 mil wires into water and found that the data for an impure specimen (R-ratio = 500) had a lower slope and were shifted to the right of the pure specimen data (R-ratio = 5000). He attributed the shift to vacancy-impurity complexing, which retarded the migration of vacancies to sinks during the quench. While it is not clear that such a mechanism is responsible for the observed data shift, this shift is qualitatively consistent with the predictions of equations 9 and 10. Cizek (53) studied the irreversible increase in the resistance of thin platinum wires quenched into air and water, and concluded that only 80% of this increase was associated with geometry changes in the specimens; the remaining 20% he ascribed to the formation of stable vacancy-impurity complexes, with oxygen being the most likely contaminant. Other "contamination" effects have been observed by the author in a separate study of the quenching of 2 mil platinum wires in superfluid helium (54) (here neither the specific contaminant nor the contamination mechanism involved was identified), and by Misek (55), whose results are discussed below in connection with specific contamination effects we observed in the annealing of 4 mil specimens in air.

Considering the data of figure 12 from the point of view of a temperature shift, we see that the data is quantitatively consistent with the prediction of equation 9: the further the line is shifted to the right, the lower, in general, is its slope. Since lines E and F are shifted from line A by nearly a constant temperature difference Δ, we can further attempt to determine if their respective slopes E_f and shifts Δ are quantitatively consistent with equation 9. Using line A as a reference line and the values of Δ obtained from figure 12, we find that the slopes of lines E and F agree to within experimental error with those predicted by equation 9. The actual values are about 0.03 eV higher than the predicted ones, but this disagreement might be associated with the faster quench speeds obtained with a QSII (lines E and F), which might raise the slopes of these lines over that of A, independent of a possible temperature shift.

In the absence of an independent means of measuring the specimen temperature directly, the occurrence of a temperature shift can only be inferred from the data.

However, an indirect means of estimating whether temperature shifts might have taken place can be obtained by plotting the current (i.e., power) used for heating a specimen against its nominal temperature. The reasoning employed is this: if all specimens are nearly identical (i.e., they have the same diameter and are not greatly contaminated with impurities) and are heated in the same environment, then the power necessary to maintain them at a certain temperature T (all specimens normalized to a standard gauge length) depends only on I^2, where I is the heating current. Thus, if two nominally identical specimens require different heating currents to obtain the same nominal temperature, they are either not at the same temperature, or are not identical.

When the heating currents are plotted against the nominal quench temperatures for the 16 mil specimens whose data is presented in figure 12, a positive correlation is seen between the two sets of data: those specimens which show the largest quenched-in resistance for the same nominal quench temperature also require the largest current to maintain that temperature; i.e., the current versus temperature curves are shifted, using line A as a reference line, by approximately the same number of degrees as are their quench data curves. In addition, specimens which yield nearly identical quench data, also yield nearly identical current-versus-temperature curves. Hence, as explained above, the existence of such an anomaly indicates either that a temperature shift has occurred or that the specimens are not identical. Since we had no independent means for measuring the temperature, let us examine in more detail the second possibility.

To what extent can the specimens be said to be "identical" in composition and geometry? With regard to the first criterion, we note that all eight 16 mil specimens were initially 99.999% pure and all but one had an initial R-ratio of 4000 or better, independent of whether it was given the longer or shorter high temperature anneal. With regard to the second criterion, we note that the heating current curves of those specimens given the longer high temperature anneals are shifted in a direction consistent with a thinning of these specimens produced by the annealing. However, changes in the diameters of these specimens obtained from actual measurements with a microscope and calculated from observed changes in the room temperature resistance before and after the anneals are too small to account for the observed shifts in their heating current curves. Thus, to within our ability to detect differences in specimen composition or geometry, the specimens appear to be identical and the hypothesis of a temperature shift appears more likely to be correct.

We shall now show that the same conclusion does not apply to the intra-specimen data shifts discussed above. For one, although these data shifts are compatible with equation 9, a temperature shift, the heating current curves are nearly identical for the original and shifted data. Thus, it seems unlikely that these data shifts are caused by temperature shifts. On the other hand, as previously noted, these specimens always showed a significant decrease in their resistance ratios between the original and shifted data. Such a decrease in the resistance ratio may indeed correspond to an increase in the specimen's impurity content. However, a single explanation (e.g., equation 10) for all of the intra-specimen data shifts is not completely satisfactory when one attempts to explain with it the data obtained with the 4 mil specimens.

In section II, we reported that 4 mil specimens annealed at temperatures greater than 1250°C yielded quite low resistance ratios--in the vicinity of 250--while anneals at lower temperatures produced R-ratios of 3000 or better (see Table II). To further investigate this phenomenon, a previously unannealed 4 mil specimen was given an isochronal anneal (using 10 minute holding times and temperature intervals of 100°C) at increasing temperatures between 100° and 1000°C. The specimen's resistance ratio was observed to increase after each annealing step to a value of 2800, until a slight decrease was observed after an anneal at 950°C. Further annealing at higher temperatures slowly decreased the R-ratio to 2650 until anneals of less than 5 minutes at 1400° and 1500°C lowered the R-ratios to 1000 and 800, respectively. Longer anneals at temperatures less than 950°C were able to restore the respective ratios from 1000 to 1400 and from 800 to 880.

Thus, it seems that the high-temperature air anneals are "contaminating" these specimens and lower temperature anneals are "purifying" them. (Similar phenomena have been reported by Misek (55), who also reported the "contamination" of "pure" 4 mil air-annealed specimens by annealing in vacuum.) However, the 4 mil specimens were initially of the same nominal purity (99.999%) as the 16 and 10 mil specimens which had R-ratios of 3000 to 9000 when annealed in air at temperatures of 1500°C or greater. In addition (see Table II), 10 mil specimens given the longer high temperature anneals showed R-ratios between two and three times greater than those given much shorter high temperature anneals; and the R-ratios of the 16 mil specimens showed no dependence on the initial air-annealing treatment. One is therefore left to conclude that (1) if annealing in air either purifies or contaminates the wires, the relation between specimen purity and resistance ratio is by no means a simple one, or (2) some interaction occurs between the specimen and its annealing atmosphere, and the interaction depends strongly upon the wire diameter (possibly associated with the larger surface area to volume ratio of the thinner specimens).

An attempt to isolate a single explanation for the above phenomena and for the observed data shifts is further frustrated when one considers the quenching data from various 4 mil specimens. Intra-specimen data shifts (i.e., shifts to the right) were frequently observed in initially "pure" (R-ratio $\geq$ 2000) 4 mil specimens. However, inter-specimen data shifts were also observed among the several 4 mil specimens used, but in one case, the initially "contaminated" specimens (R-ratio $\approx$ 250) yielded data shifted slightly <u>to the left</u> of the original "pure" specimen data and with a slightly lower slope. A possible explanation for this inconsistency may lie in the fact that the heating current-temperature curve for the "contaminated" specimen was shifted from that of the "pure" specimens in a direction consistent with a temperature shift of nearly 50°C to the left of the "pure" specimen, thereby resulting in a much smaller net shift in the data. Thus, it seems possible in some cases that both a temperature shift and impurity effects are responsible for the shifts in the data.

In summary, it appears that the 16 mil inter-specimen data shifts are fairly consistent with the hypothesis of a temperature shift, while most of the intra-specimen shifts are more likely to be associated with impurity effects. However, the sources of either phenomenon are obscure, and until they are investigated directly (i.e., an alternate means of temperature measurement and an explicit analysis of specimen impurity content), we feel that a positive conclusion as to the cause of these shifts is unwarranted.

APPENDIX B

CHANGES IN SPECIMEN PARAMETERS AND THE MAGNITUDE OF LIQUID QUENCHING STRAINS

Throughout a specimen's lifetime its room temperature resistance in the annealed state, R_{20}, and its vacancy-free base resistance in liquid helium, R_B, were periodically measured. Small changes in both values were often observed and were used to make corrections to the previously obtained data. For the 16 and 10 mil specimens, the changes in R_{20} were both positive and negative and were usually smaller than a few tenths of a percent over a specimen's lifetime. However, for specimens that were repeatedly liquid-quenched from high temperatures, R_{20} tended to increase. The 4 mil specimen whose data is presented in figure 20 showed an increase in R_{20} of about 5% during its lifetime. Long-term changes in a specimen's vacancy-free base R_B were nearly always positive and were generally larger for the smaller wire diameters. For most of the 16 mil specimens, the increase in R_B over a specimen's lifetime was less than 2μΩ or, equivalently, $\Delta R_B/R_{20}$ = 5×10^{-5}. However, increases in R_B as large as $\Delta R_B/R_{20}$ = 2×10^{-4} were observed in some water-quenched 10 mil specimens and gas-quenched 4 mil specimens. In most cases, the increases in R_B could not be directly associated with geometry changes in the specimen, since no comparable increase was observed in R_{20}, and the resulting resistance ration R_{20}/R_B was seen to decrease significantly.

In addition to the periodic measurements of R_{20} and R_B discussed above, more precise measurements of R_{20} were made in order to determine the magnitude of strains produced in liquid quenches. For, if a specimen is plastically strained during a liquid quench, the resulting strain, ε, can be detected by the change in its geometry and, therefore, its resistance. In particular, if the strain is characterized by a uniform lengthening and thinning of the specimen after the quench (with no change in the specimen volume), then the strain is given by $\varepsilon = 1/2\ \frac{\Delta R}{R}$, where R is the specimen's (vacancy-free) resistance at some fixed temperature. Since ε is likely to be quite small (10^{-3} or less), a more sensitive method for detecting changes in the specimen's resistance than those employed so far had to be used. Also, since changes in the resistance associated with geometry changes in the specimen increase with increasing measuring temperature, it is advantageous to choose a reasonably high measuring temperature; e.g., room temperature or higher.

Both of these conditions were reasonably satisfied by the use of the constant temperature bath employed in the Mattheissen's rule experiments described in appendix D. With this apparatus, fractional changes in the specimen's resistance at 30.5°C could be detected with an accuracy of better than 1×10^{-4}. The procedure employed was to quench a 16 mil specimen into water from temperatures between 20 and 700°C (where no measureable vacancy resistance should be quenched in) and to measure its resistance in the bath at 30.5°C before and after the quench. The resultant changes in $R_{30.5}$ for any single quench were found to be less than or equal to the measuring accuracy, 1×10^{-4}. Cumulative increases in $R_{30.5}$ for 13 consecutive water quenches in this same temperature range amounted to less than 4×10^{-4}, or approximately 3×10^{-5} per quench.

Higher temperature quenches appeared to produce larger increases, however. Sixteen mil specimens quenched from between 1200 and 1700°C and given a short cleansing anneal showed increases in $R_{30.5}$ ranging from 1 to 5 x 10^{-4} per quench. In either case, the magnitude of the induced strain is small enough to avoid significant vacancy losses as determined by Jackson (49), who argued that the presence of strains during a quench will, at all but the lowest quench temperatures, decrease the number of vacancies quenched into the lattice.

Finally, in order to ascertain the effects of quenching strains on the quenched-in resistance itself, we quenched other 16 and 10 mil wires into water from quench temperatures between 20 and 650°C, and measured the base resistance R_B in liquid helium before and after each quench. Again, in this temperature range, the equilibrium vacancy resistance is too small to be detected by our measuring apparatus. Thus, any changes observed in R_b must be due to changes in the wire's geometry or defect structure induced by liquid quenching (e.g. the production of "strain vacancies"). The observed fractional changes in R_B after quenching were found to be less than 1%, the limit of our measuring accuracy. Since one does not expect strain effects to increase appreciably with temperature (49), it appears that the effects of liquid quenching strains on our low-temperature data should be minimal.

APPENDIX C

REVIEW OF PREVIOUS QUENCHING EXPERIMENTS ON PLATINUM

In section IV we presented data for water quenches of 16 and 10 mil wires which yield a value of 1.23 ± .07 ev for the vacancy formation energy in platinum. Such a value agrees well with that of several of the earliest studies on quenched platinum (see Table I). It is considerably lower however than the value of 1.50 ev obtained by Jackson (32), who concluded that the previous quenching studies could have obtained such low values for E_f because of inherent systematic errors. Specifically, the thin specimens used in the earliest studies may have been contaminated with impurities, or had been strained considerably by rapid quenching into water. Also the temperature range investigated in these studies is one in which the loss of vacancies due to insufficient quenching rates can be significant. Since, in the present study, we have attempted to follow

Jackson's procedure, but have obtained results consistent with those of the earliest studies, we feel it is useful to review the results of previous quenching studies--especially with respect to the possibility of systematic errors as discussed above.

In Table V we have listed the pertinent data for several previous quenching studies, including that of Jackson, and will now review them according to Jackson's criteria, starting with that of specimen purity.

All of the studies previous to Jackson's reported using 99.999% pure platinum--the same as that of Jackson--except study A, which reported only that the residual resistance ratio of its wires was 560. Thus, the most likely source of any contamination of the specimens must have occurred during preparation, annealing or quenching. The occurrence of such contamination would have been most easily detected by changes in the specimen's residual resistance ratio, $R_{273\ K} / R_{4.2\ K}$. However, in studies B, C, and D, measurements of the specimen's vacancy-free resistance were made at temperatures no lower than 77 K, a temperature too high for sensitive measurement of small

TABLE V

A LIST OF SEVERAL PERTINENT EXPERIMENTAL QUANTITIES FOR PREVIOUS QUENCHING STUDIES ON PLATINUM

Investigator(s)	Specimen Diameter (mil)	Type of Quenching Used	Initial Quench Speed (°C/sec)	[or] Cooling Time (sec)	Quench Temperature Range (C)	Measuring Temperature (K)	E_f	Ref.
A. Lazarev and Ovcharenko(1955)	4	air			750-1200	4.2	1.2	25
	2							
B. Bradshaw and Pearson(1956)	8	water	30,000	0.020	950-1700	77	1.4 ±.10	26
	4	"		0.0065				
	2	"		0.0024				
	1	air						
C. Ascoli *et al.* (1958)	4	water		0.035±.005	850-1600	77,293	1.23	27
	2.8	"		0.035±.005				
	1.6	air		0.1				
D. Bacchella *et al.* (1959)	4	water		0.035	850-1600	288	1.20 ±.04	28
	1.6	air		0.1				
E. Misek(1964)	2	air	6,000-14,000		600- 900	4.2	1.24	30
F. Jackson(1965)	16	water	15,000-40,000		700-1750	4.2	1.51 ±.04	33
G. Baumgarten *et al.* (1968)	4	flowing gas	20,000		700-1100	77	1.46 ±.02	33
H. Present study (fast-quench data)	16	water	20,000-45,000		700-1600	4.2	1.23 $\pm.07_{ev}$	
	10	water	20,000-45,000					
	4	air	2,300-4,000				1.30 $\pm.05^{ev}$	

or moderate contamination effects. Thus, while each of these three studies reports changes in the specimen's vacancy-free resistance after a number of quenches they do not provide a sensitive means for discriminating between resistance changes associated with geometry changes or with impurity effects. As noted in Appendix A, Misek (56), Cizek (54), and Jackson (32) have observed effects in quenched or annealed platinum wires which are accompanied by significant changes in the R-ratio of the specimens. However, the exact mechanism behind such "impurity effects" and their influence on the values of E_f determined from such studies have yet to be determined.

The quench speeds or quench times reported for water quenches in studies B, C, and D, appear to be equal to or greater than those reported by Jackson in his study--presumably a consequence of the thinner wires used in all of the above experiments--but, without direct knowledge of the sink densities of the specimens used, one cannot make a direct comparison of the respective quench data for specimens of different diameters. However, according to the findings of Jackson and of the present study, it is possible that these studies could still be adversely affected by insufficient quenching rates, because of the relatively high temperature range ($T_q \geq 1000°C$) in which the bulk of the quenches were done. Specifically, as both Jackson (32) and the present study have shown, the quenched-in resistance appears to be relatively insensitive to the quenching rate for quench temperatures lower than about 1000°C. At higher temperatures, however, the quenched-in resistance begins to fall off more rapidly with temperature for even the faster quenching rates. Such behavior is reflected in the curvature (i.e. the departure from linearity) in the logarithmic plot of ΔR_Q versus $1/T_q$ at the higher quench temperatures. Such curvature is evident throughout nearly the whole temperature range of the Bradshaw and Pearson data (study B). Because of this and because of the larger scatter in their data, we believe that their lower estimate of E_f (1.30 eV) to be the most justified by the data. In this regard, the data of studies C and D are rather surprising in that they report nearly linear quench data over an even larger temperature range than that of

Bradshaw and Pearson, despite the slightly longer quench times reported in the former studies. However, the values of E_f obtained in studies C and D (1.23 and 1.20 ± .04 eV respectively) do not disagree substantially with Bradshaw and Pearson's lower estimate, and agree quite closely with the value of 1.24 eV determined by Misek, and the 1.2 eV of Lazarev and Ovcharenko. In particular, these latter two studies (A and E in the table) are notable in that (a) they quenched either 2 or 4 mil wires in air, eliminating the possibility of liquid quenching strains; (b) the bulk of the quenches were done below 1000°C, reducing the possibility of vacancy losses caused by insufficient quenching rates; (c) their resistance measurements were made at 4.2K, insuring adequate measuring sensitivity. The major deficiency of both of these two studies is their limited amount of data. The same deficiency is present in study G, which gives data for the quenched-in resistance at only 3 quench temperatures.

The effects of liquid quenching strains on the quenched-in vacancy concentration would be most significant in studies B, C, and D, where rather thin wires were quenched into water, and these studies do report phenomena likely to be produced by significant quenching strains: increases in the quenched-in resistance independent of quench temperature (study C), and increases in the residual resistance of the wires after a number of quenches, attributed to changes in their dimensions (studies B and C). However, these studies give little or no quantitative data from which the magnitude of liquid quenching strains can be deduced. On the other hand, all three studies include complementary air quench data that agrees well with that of the water quenches. Also, the values of E_f obtained from the studies B, C, and D are in good agreement with those of studies A and E, despite the different quenching methods employed in both groups of studies.

In summary, it appears that all of the platinum quenching experiments done before that of Jackson could have been affected to some extent by the systematic errors produced by impurities, insufficient quenching rates, or liquid quenching strains. In most cases, it is not possible to determine the extent to which any of these were operative in these five early studies because of the lack of data related directly to them. Considering, however, the amount of diversity included among these studies (wire diameters ranging from 1 to 8 mil, both air and water quenches, and quench data for both the high and low-temperature ranges) and the relatively good agreement in the values of E_f obtained in studies A, C, D, and E, it is not obvious that the differences in the values of E_f obtained from them (1.20-1.24 eV) and from Jackson's study (1.50 ± .04 eV) are due solely to the occurrence of the above-mentioned systematic errors as proposed by Jackson. From our discussion in Appendix A, it appears that the annealing treatment used in any platinum quenching study may be a criterion of equal or greater importance than those listed above. Again, there is little quantitative information regarding the annealing treatments used in any of the published studies (except E and F) listed in Table V from which meaningful comparisons can be made.

APPENDIX D

VACANCIES AND MATTHEISSEN'S RULE IN GOLD AND PLATINUM

When electrical resistance measurements are used in conjunction with quenching experiments, two basic assumptions related to the vacancy resistivity are usually made. The first is that quenched-in resistivity is directly proportional to C_v, the quenched-in monovacancy concentration; i.e.

$$\rho_v = \rho_i C_v \qquad [3]$$

where ρ_i is the resistivity per unit concentration of single vacancies. This assumption is the more crucial one since it directly affects the interpretation of quenching experiments. Thusfar, very little has been done to investigate the validity of equation 3 directly, but it is believed to be a good approximation except in the case of extensive vacancy clustering (18).

The second assumption--Mattheissen's rule--is that ρ_v is independent of the temperature at which the quenched-in vacancy concentration is measured; i.e.

$$\rho(T) = \rho_L(T) + \rho_v \qquad [11]$$

Here, $\rho(T)$ is the resistivity of the specimen at absolute temperature T, and $\rho_L(T)$ is the normal, temperature-dependent, lattice resistivity of a pure, vacancy-free specimen. The assumption of the validity of equation 11 should, however, pose no serious problems for quenching experiments, since, in practice, all measurements of ρ_v are made at the same highly-reproducible temperature (e.g. in liquid helium at 4.2 K). And, since resistivity measurements give C_v only to within a constant, the determination of E_f via equation 4 should not be affected by a temperature dependence in ρ_v. Nevertheless, very little is known about the validity of Mattheissen's rule for vacancies in quenched metals. And what information is available is not internally consistent.

In 1965 Bass (56) showed that there was good agreement between his measurements at 4.2°K of the resistivity quenched into 0.016" diameter gold wires and similar measurements by Bauerle and Koehler (12) at 77°K and by Emrick (57) at 273°K. He concluded that there appeared to be little deviation from Matthiessen's rule in the resistivity of vacancies in gold. Recently, however, Conte and Dural (58) reported observing an increase by a factor of four in the resistivity quenched into a 0.004" diameter gold wire as the temperature of the wire was raised from 4.2°K to 303°K. In view of this disagreement we decided to investigate deviations from Matthiessen's rule in gold and platinum by measuring at 4.2°K and 303°K the excess resistivity retained in 0.016" diameter gold and platinum wires and 0.008" diameter gold wires quenched into water from a series of temperatures.

The high temperature measurements were made in a well-stirred bath of either kerosene or distilled water (with similar results), which served to maintain the relative resistance of the wires constant to within $\delta R/R_{20°C} \gtrsim 1 \times 10^{-4}$ over a period of many hours. Here δR is the maximum resistance variation, and $R_{20°C}$ is the resistance of the well annealed wire at 20°C. For most of the data, the cleansed (vacancy-free) resistances were measured at 4.2 and 303°K before and after each quench. However, in some cases two or three quenches were made between measurements of the cleansed resistance. In these cases, suitable averages of the pre- and post-quench cleansed resistances were subtracted from the resistance of the quenched wire to obtain the quenched-in resistance.

Originally, only 0.016" diameter platinum and 0.008" diameter gold wires were quenched. However, quenching stresses often produced substantial changes in the geometry of the 0.008" diameter wires, making it difficult to obtain precise data at 303°K. Therefore, additional quenches were made with a 0.016" diameter gold wire, in which smaller geometry changes were expected, and, in fact, observed.

The quench data for three independent platinum wires and one 0.016" and two 0.008" diameter gold wires are shown in figure 28. (To remove the effects of differing specimen geometries, the measured resistances have been divided by the resistance of the same wire at 20°C.) The precision of the helium temperature measurements was

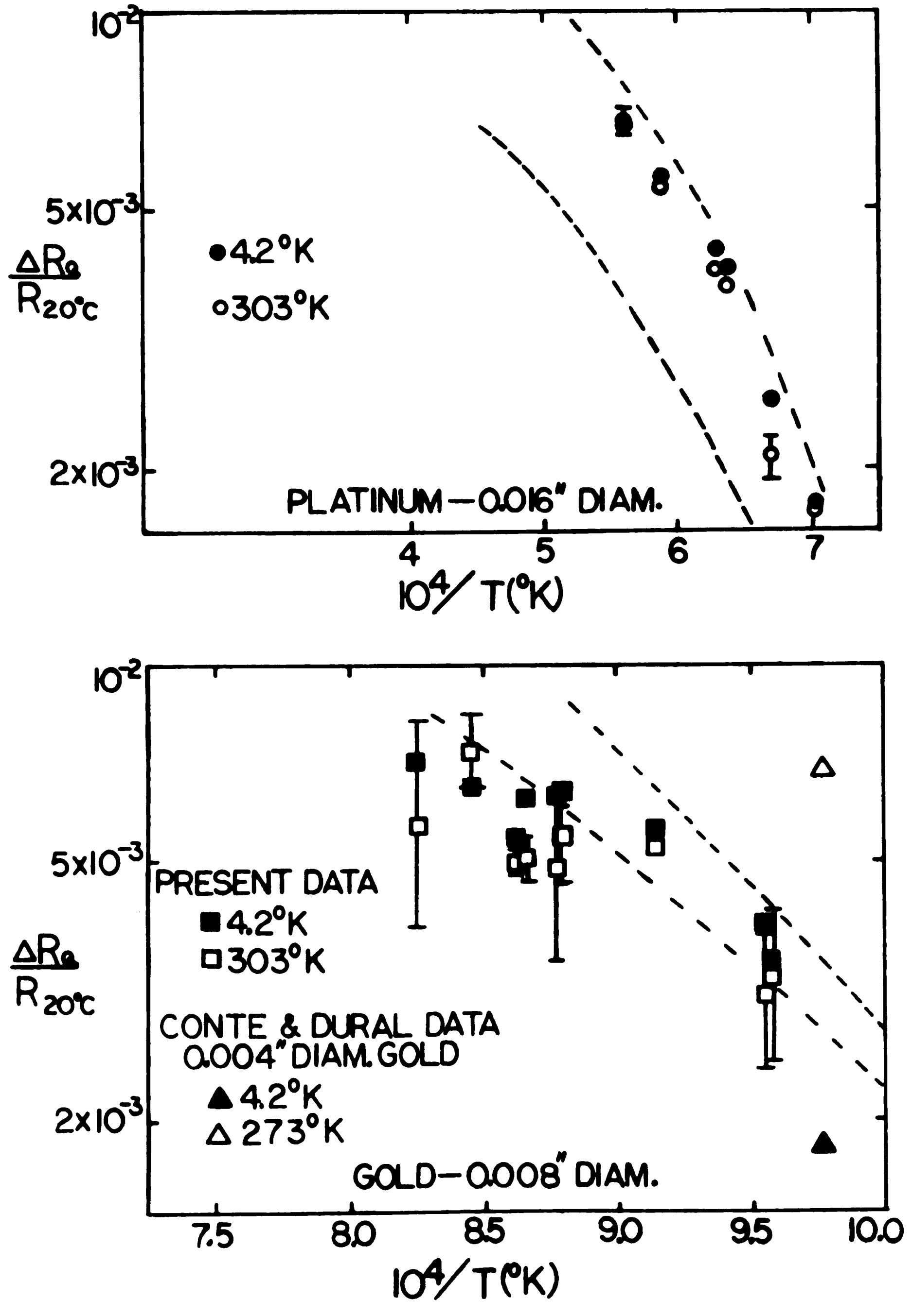

FIG. 28. — THE RESISTANCE QUENCHED INTO GOLD AND PLATINUM WIRES AS A FUNCTION OF BOTH THE MEASURING TEMPERATURE AND INVERSE KELVIN QUENCH TEMPERATURE. THE DASHED LINES INDICATE THE RANGE OF QUENCHED-IN RESISTANCE PREVIOUSLY OBTAINED BY BASS (1964) ON GOLD AND IN THE PRESENT STUDY (SECTION IV) ON PLATINUM.

better than the size of the symbols shown in the figure. For the data at 303°K, the error bars indicate the possible maximum and minimum values of the quenched-in resistances associated with changes in the cleansed resistances produced by changes in specimen geometry. These error bars are generally large for the 0.008" diameter wires, but usually no larger than the symbols for the 0.016" diameter wires. The remaining sources of error lead to an additional uncertainty of about $\delta R/R_{20°C} = 2 \times 10^{-4}$ for each 303°K data point.

To test for vacancy annealing at 303°K, repeated measurements at 4.2 and 303°K were made. Corresponding decreases in the resistances measured at both temperatures confirmed the existance of minor annealing in gold quenched from high temperatures. No annealing was observed in platinum. To further test the effects of vacancy annealing on deviations form Matthiessen's rule, isochronal anneals were performed on a platinum wire quenched from 1300°C and on a 0.008" diameter gold wire quenched from 870°C. Measurements at 4.2 and 303°K of the fractional resistance losses during the anneals indicated no large deviations from Matthiessen's rule in either gold or platinum.

As can be seen from figure 1, we do not reproduce the large deviations from Matthiessen's rule reported by Conte and Dural. To within our experimental uncertainty, we find no increase in quenched-in resistance with increasing measuring temperature for either gold or platinum. It may be that the large deviation seen by Conte and Dural was due to geometry changes associated with quenching strain in their thin specimen.