

should be present. They are of course unoccupied, lying above the Fermi level. They should be observable with high-resolution electron

transmission through thin films,⁷ with inelastic low-energy-electron diffraction (LEED), and as resonances of elastic LEED.⁸

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Effect of Pressure on Vacancy Concentrations in Platinum[†]

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The excess electrical resistivity quenched into platinum as a function of pressure (up to 6 kbar) and of quench rate has been measured. The activation volume for the formation of vacancies was found to be 6.4 ± 0.7 cm³/mole (0.70 atomic volume). Preliminary results on fractional vacancy loss during quench as a function of quench rate are consistent with previous conclusions that vacancy clustering is negligible in platinum.

I. INTRODUCTION

The mechanism for the low-temperature recovery of excess electrical resistivity in platinum after a quench from high temperature is much simpler than in the noble metals or aluminum.¹ As a preliminary to studying the loss mechanism during the quench, we have measured the excess electrical resistance quenched into platinum from a fixed high temperature as a function of pressure and of quench rate. Since the basic theory, apparatus, and techniques have been described earlier,² only the relevant differences and the results will be presented here.

II. EXPERIMENTAL

Specimens were fabricated from 0.075-mm-diam reference-grade platinum wire supplied by the Sigmund Cohn Corp., Mt. Vernon, N. Y. Since it was impractical to make electrical-resistance measurements at liquid-helium temperature, changes in the specimen resistance relative to a reference specimen were measured with standard bridge arrangement.³ Potential leads of 0.013-mm-diam platinum wire, resistance welded to the larger wire, defined the specimen and reference

regions. The roughly 3 cm lengths of the specimen and reference regions were within 0.5% of each other.

The specimen and reference were given the cleansing heat treatment in air described by Jackson,⁴ with one exception. The specimen mount precluded the water quenches and aqua-regia etch after the 1500 °C anneal. The mount also made it impossible to determine the liquid-helium-temperature resistance of the specimen after the cleansing heat treatment. Room-temperature to liquid-helium-temperature resistance ratios measured for samples taken from the same section of stock wire as the specimen and prepared in the same way were about 3300. A spectrographic analysis of the stock wire by Jarrell-Ash, Waltham, Mass., is listed in Table I.

After the initial heat treatment, the specimen resistance was measured in air at atmospheric temperature and pressure. The values, corrected to 0 °C, were typically 0.5 Ω. The specimen mount was placed in the high-pressure vessel where it remained for the duration of the experiment. The pressure medium was either ultra-high-purity (UHP) argon or UHP argon-5% oxygen. The reference pressure of the system was 1700 psi, at

TABLE I. Spectrographic analyses of samples.

All metallic impurities were reported as not detected (ND) except for the following:							
	Mg	Si	Ca	Cr	Fe	Cu	Ag
Stock	C/B	A	B	ND	A	B	B
P12 (After etch)	B	D	B	B	B/A	B	B
Key to atomic concentrations of impurities							
A = $< 10^{-6}$				C = $10^{-5} - 10^{-4}$			
B = $10^{-6} - 10^{-5}$				D = $10^{-4} - 10^{-3}$			

which value all subsequent resistance measurements and cleansing heat treatments were made. The treatments after each quench consisted of anneals for 5 min at 1050 °C, 10 min at 700 °C, and 5 min at 500 °C. The intent of these treatments was to return the specimen to a vacancy-free state.

In determining the quench temperature at elevated pressures, a correction must be made to the resistivity-vs-temperature scale. For the gold and aluminum quenches² we had available the high-temperature-high-pressure data of Bourassa *et al.*⁵ Unfortunately, their pressure vessel failed before they completed their measurements on platinum. To approximate $R(T, p)$, the resistance as a function of temperature T and pressure p , we assumed it to be of the form $r_T(p)R_p(T)$, where $r_T(p)$ is the pressure coefficient of resistance at T and $R_p(T)$ is the temperature dependence of the resistance at p . Data supplied by Johnson, Mathey, Inc. indicate that for $p = 1$ atm, $R_p(T) = R_0(1 + 0.00397795t - 5.875 \times 10^{-7}t^2)$, where R_0 is the 0 °C resistance and t is the Celsius temperature.

We measured the room-temperature pressure coefficient $r_{25^\circ\text{C}}(p)$ for our specimen material and found it to be consistent with Bridgman's⁶ 0 and 100 °C data. We fitted Bridgman's 100 °C data with the form $r_{100^\circ\text{C}}(p) = 1 - 0.0018983p + 5.1 \times 10^{-6}p^2$, where p is the pressure in kbar. Although $R_p(t)$ is nearly pressure independent,⁶ $r_t(p)$ is not temperature independent. Thus our temperature scale, defined by $R(t, p) = r_{100^\circ\text{C}}(p)R_{1\text{atm}}(t)$, is most likely in error at the temperatures from which the quenches are made. When experimental data for $r_t(p)$ at these high temperatures become available, corrections for the actual quench temperature can readily be made. When such a correction is applied in the case of gold,² the temperature is decreased 6–8 °C at 700 °C and 6 kbar or about –0.7% at 73% of the melting temperature T_M .

Our temperature controller⁷ maintains the resistance of the entire 0.075-mm-diam wire at a constant value. The specimen temperature is deter-

mined from the voltage measured between the potential leads with an L&N K-3 potentiometer and the specimen current measured with a calibrated $\frac{1}{4}\%$ Weston dc ammeter to a precision of $\pm 2^\circ\text{C}$. However, convection currents can cause the temperature of one region of the wire to differ from another, even though the total resistance is constant. Specimen voltage fluctuations measured with an oscilloscope indicate short-term temperature fluctuations of 10 °C. These fluctuations are random and unresolvable by the dc apparatus. The actual quench temperature may be in error by as much as 12 °C and is the major source of experimental error.

The temperature controller adjusts the current during the quench so that the temperature decreases linearly; i. e., $T(t) = T_Q - t/\tau$, where T_Q is the quench temperature, t is the time from the beginning of the quench, and $\tau = -\dot{T}^{-1}$ is the reciprocal quench rate. Even for the fastest quenches, $\dot{T} \approx -10^4$ °C/sec, this expression is valid down to 700 °C. Quenches were made for T_Q near 1050 and 1200 °C.

III. RESULTS

In Fig. 1 the excess resistance ΔR quenched in from 1065 °C is shown as a function of reciprocal quench rate for a series of pressures. ΔR has been normalized by R_0 , the specimen resistance at 0 °C, so that comparisons with other specimens can be made. Since the quench temperatures were low (relative to the melting temperature T_M), the quench rates constant, and the fractional vacancy losses during the quench small, a linear extrapolation⁸ to infinite quench rate was used to determine $\Delta R_\infty/R_0$, where ΔR_∞ is the resistance that would

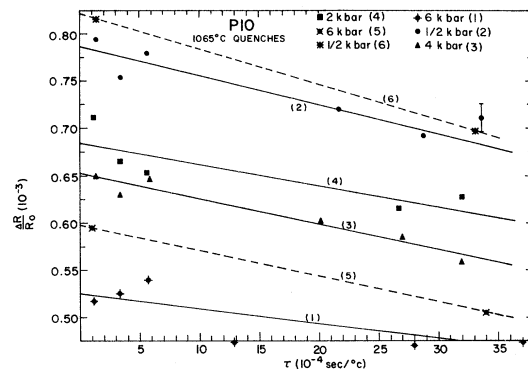


FIG. 1. Normalized electrical resistance ΔR quenched into platinum as a function of reciprocal quench rate τ at various pressures. The solid lines are weighted least-squares fits to the data. The dashed lines are hand drawn, since for these isobars there are only two data points. The numbers identifying the isobars indicate the sequence in which they were made. The resistance of specimen P10 at 0 °C, 1 bar, R_0 , was 0.5141 Ω .

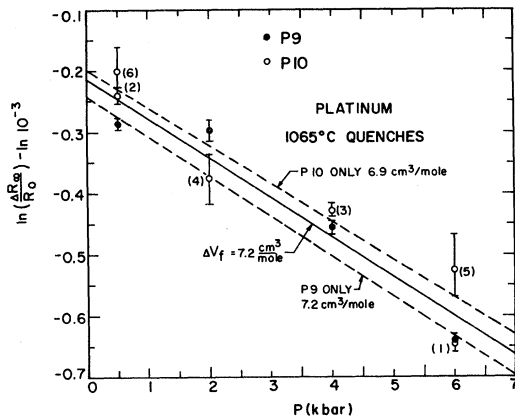


FIG. 2. Natural logarithm of normalized electrical resistance quenched into platinum at infinite quench rate as a function of pressure. The open circles are the intercepts of the isobars in Fig. 1 and are numbered correspondingly. The solid circles are for specimen P9, whose value of R_0 was 0.5582 Ω . The dashed lines are weighted least-squares fits for the individual specimens and the solid line is the weighted least-squares fit to all the data. The indicated formation volumes are determined from the slopes of the lines.

be quenched in at infinite quench rate.

Figure 2 is an example of the pressure dependence of such intercepts for two different specimens. The straight lines are least-squares fits to the data, with each point weighted by its statistical uncertainty. If we assume that the equilibrium defect concentration c at the quench temperature is proportional to ΔR_∞ , then the slopes of these lines are $(\partial \ln c / \partial p)_{T_Q}$. The formation volume for the defects ΔV_f at T_Q is given by² $\Delta V_f = -kT_Q$

$\times (\partial \ln c / \partial p)_{T_Q}$. Values of ΔV_f inferred from Fig. 2 and other experimental data are listed in Table II along with the best value for this series of experiments. Also shown for comparison are the formation volumes of vacancies in gold and aluminum.

IV. DISCUSSION

Since the ratio of the quench to melting temperatures is low, the value of ΔV_f is the single-vacancy value, unless the divacancy binding energy is in excess of the highest reported.^{1,11} In thermal equilibrium between single and divacancies, the divacancy concentration c_{2v} is given by¹² $c_{2v} = 6 \times (c_{1v})^2 \exp(E_{2v}^B/kT)$, where c_{1v} is the single-vacancy concentration and E_{2v}^B is the divacancy binding energy. For $E_{2v}^B = 0.4$ eV⁹ and $T = 1050^\circ\text{C}$, $c_{2v}/c_{1v} \approx 10c_{1v}$ or less than 10^{-3} . Whereas this relative concentration could modify defect annealing kinetics because of the high divacancy mobility, it would have a negligible effect on the defect volume. Thus we find that the ΔV_f values for the 1050 and the 1200 $^\circ\text{C}$ quenches agree within experimental error.

Only by quenching from near the melting point might a divacancy contribution to ΔV_f be detected. Attempts to quench from higher temperatures usually burned out the specimen, but four successful quenches were made from 1575 $^\circ\text{C}$. However, the prequench anneal *increased* the background resistance rather than returning it to its original value, so that the results were meaningless. No purity analysis was made on that specimen so it is not known if the resistance increase was caused by impurities or by oxidation and evaporation of platinum from the specimen's surface.¹³

Numerically, the values of $\Delta R_\infty/R_0$ extrapolated to atmospheric pressure ranged from (0.6 to 0.8)

TABLE II. Experimental results for individual specimens.

Specimen	ΔV_f^a (cm ³ /mole)	T_Q ($^\circ\text{C}$)	T_Q/T_M	Pressure gas	$\Delta V_f/V_0$
P4	6.1 ± 1.0	1200	0.72	pure A	0.67
P6	7.6 ± 1.2	1200	0.72	A-10% air	0.83
P9	7.2 ± 0.7	1065	0.65	A-15% air	0.79
P10	6.9 ± 0.9	1070	0.66	A-6% O ₂	0.76
P12	6.3 ± 1.0	1063	0.65	A ~ 5% O ₂	0.69
P16	6.7 ± 1.0	1061	0.65	A ~ 5% O ₂	0.74
P18	5.9 ± 0.4	1010	0.63	A ~ 5% O ₂	0.65
Best value this experiment	6.4 ± 0.7				0.70
Gold ^{b,c,d}	6.8 ± 0.4	} 720 640	0.74	A	0.65
Aluminum ^{b,c}	6.38 ± 0.15		420		

^a ΔV_f is the formation volume, T_Q is the temperature from which the quenches were made, T_M is the melting temperature at atmospheric pressure, and V_0 is the atomic volume of the material.

^bReference 2.

^cReference 9.

^dReference 10.

$\times 10^{-3}$ for the 1050 °C quenches and (1.8 to 2.0) $\times 10^{-3}$ for the 1200 °C quenches listed in Table II. These ranges are in agreement with those determined by more conventional methods.^{1,14,15} In runs of 40–50 quenches, the base specimen resistance increased by an amount less than that quenched in from 1050 °C. Polák and Kunz¹³ have reported a similar resistance shift (also noted much earlier by Bradshaw and Pearson¹⁶) of air-quenched specimens which were absent in an argon atmosphere. They attribute the increase to a loss of platinum by oxidation. Jackson⁴ notes that anneals in air improve the residual resistivity ratio compared with anneals in argon. We cannot tell whether our changes in resistance are of the former geometric origin or of the latter volume-impurity origin.

Specimen P12, which was quenched 47 times from 1050 °C in an UHP argon–5% oxygen atmosphere, was spectrographically analyzed by Jarrell-Ash, Waltham, Mass. The results are shown in Table I. Prior to the spectrographic analysis the specimen was observed under a scanning electron microscope (SEM). In addition to the typical bamboo-grain structure, bands of silicon-containing material were observed on some regions of the surface. This may account for the fact that the $\frac{1}{2}$ -kbar intercepts for P12 tended to decrease in value as the isobars were repeated to check reproducibility. The 6-kbar isobars did not exhibit such a shift. On other specimens shifts in intercepts occurred, but they were random and could be explained by slight changes in quench temperature. Jackson has pointed out that quenched-in resistance *increases* with increasing impurity content in platinum.¹ Since the SEM results showed that at least some surface impurities survived the aqua-regia etch, the spectrographic analysis cannot be taken as an indication of *bulk* purity. Controlled doping experiments will therefore be performed to see if the P12 results are attributable to a pressure-dependent vacancy-impurity interaction. Examination of other specimens with a metallurgical microscope did not reveal surface

structures to the extent shown by the SEM.

In the cases of gold and aluminum, it was possible to detect a pressure dependence of the fractional loss of vacancies during the quench. Difficulties in temperature control and measurement at the high temperatures required for platinum masked any such effect. However, had the effective motional volume been as large as $0.3V_0$, where V_0 is the atomic volume, such an effect should have been resolved. In aluminum and gold an activation volume for motion of vacancies, ΔV_m , of $>0.25V_0$ was derived² when the model for the pressure effect on fractional vacancy loss during quench was that of single vacancies migrating to a fixed concentration of sinks whose efficiency was pressure independent. Since ΔV_m is $0.15V_0$ in gold¹⁷ and $0.19V_0$ in aluminum,¹⁸ these high values of ΔV_m from the simple model were taken as evidence that vacancy clustering was also occurring during quenches in these materials. The lack of such a large pressure effect in platinum is consistent with the inference that negligible vacancy clustering occurs during the quench, since little occurs during anneals after quench.¹ Further attempts will be made to improve the temperature resolution to set a better upper limit on the effective volume for vacancy loss during quench.

We have determined that the formation volume of single vacancies in platinum is $6.4 \pm 0.7 \text{ cm}^3/\text{mole}$. No evidence has been found to conflict with the previous inferences that vacancy clustering does not occur in platinum.

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PHYSICAL REVIEW B

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Role of Generalized Wannier Functions in the Effective-Hamiltonian Formalism for Magnetic Fields

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Generalized Wannier functions appropriate to magnetic fields are constructed by group-theoretic methods for nearly free electrons. A one-to-one correspondence is indicated with the zero-field band states. The diagonal elements of the effective Hamiltonian are discussed and are shown to resemble closely the energy-band function $E(\vec{k})$ when expressed in the basis set of these Wannier functions.

I. INTRODUCTION

The effective-Hamiltonian approach to the study of conduction electrons in metals with applied magnetic fields has been fruitful in explaining experimental results. This success, to a large measure, can be attributed to the fact that an expansion of the effective Hamiltonian in powers of the magnetic field has as its leading term an operator which can be easily related to the field-free band structure.¹ The terms of higher order do not appear essential for agreement with experiment. The convergence of the series is, however, yet to be demonstrated.

Wannier functions and generalizations of Wannier functions provide the most convenient basis set for considerations involving the effective Hamiltonian.²⁻⁵ This is because the localization of the functions compensates for the unboundedness of the vector potential. The nature and validity of the approximations used in the effective-Hamiltonian formalism is closely connected with whether or not it is possible to construct Wannier functions, appropriate for magnetic fields, which bear a close resemblance to the field-free Wannier functions, and which reduce to the field-free Wannier functions as the magnetic field is reduced to zero.

The extreme-tight-binding limit is well known from the early work of Peierls.⁶ In this case, the Wannier functions are simply atomic orbitals

modified by a field-dependent phase factor.

In a previous work,⁷ we examined the perhaps more difficult case of the nearly-free-electron limit. This paper contains a detailed discussion and expansion of those results. Section II contains a step-by-step construction of a Wannier function using plausible, though not rigorous, arguments. In Sec. III the results of Sec. II are incorporated into a more general group-theoretical result. Section IV is devoted to a discussion of higher bands. Section V contains concluding remarks.

II. CONSTRUCTION OF A LOCALIZED FUNCTION FROM FREE MAGNETIC STATES

The ordinary Wannier functions are defined from the Bloch functions by the relation

$$a^j(\vec{r}) = \int d\vec{k} e^{i\phi(\vec{k})} b_k^j(\vec{r}),$$

where the integral is over the first Brillouin zone in the reduced zone picture, j is a band index, and $\phi(\vec{k})$ is an arbitrary phase. The subspace spanned by the Bloch functions from the j th band is also spanned by the set of translated functions $T(\vec{R}_n)a^j(\vec{r})$, where \vec{R}_n runs over all lattice translations of the real lattice. These functions are, in principle, localized for the proper choice of $\phi(\vec{k})$. Clearly, there is a lack of uniqueness due to the phase. As will be seen, this lack of uniqueness is a much more serious problem in the magnetic case where degeneracies are a natural consequence