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Formation volume of vacancies in platinum quenched under high pressure

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The effect of hydrostatic pressures up to 8 kbar on the electrical resistance quenched in platinum has been studied. The formation volume of vacancies V^F was obtained under experimental conditions that minimized necessary corrections due to vacancy interactions and vacancy losses during the quench, as well as various uncertainties in the quench temperature. In particular, special care was taken to monitor the quench temperature accurately by using a specific calibration for the variation of resistance against pressure. The fractional measured value of V^F at 800 °C is 0.67 ± 0.03 atomic volume. Previously published results are reviewed and reanalyzed with the help of the new calibration data.

I. INTRODUCTION

The formation volume of vacancies in metals is of great interest because it is directly connected to the atomic relaxations which occur around a vacant site. From its measurement, information can be derived concerning interatomic potentials and the accuracy of atomistic models.

Most experimental studies have been based on the measurement of the variation of the equilibrium vacancy concentration with pressure, as described by the classical thermodynamic expression

$$c(T,p)=c_0\exp[-(U_V^F+pV_V^F)/kT]\ ,$$

where U_V^F and V_V^F are, respectively, the energy of formation and the volume of formation of vacancies. The relevant concentrations are measured in the quenched condition, using electrical-resistivity measurements.

Several investigations in this field have dealt with gold and aluminium.[1-3] More recently, platinum has been studied also.[4-6] In this metal, results appear to be rather scattered, ranging between 0.58 atomic volume[6] and 0.76 atomic volume.[5] We have conducted a new determination of this formation volume under experimental conditions capable of eliminating or minimizing a number of possible sources of error. In particular, we have taken into account the influence of temperature on the pressure coefficient of resistance involved in the evaluation of the quench temperature. We therefore have made a specific calibration in the high-temperature–high-pressure domain. Earlier formation volume data for platinum[4,5] are reanalyzed with the aid of the new calibration curves.

II. EXPERIMENTAL CONDITIONS

Specimens were 0.070-mm-diam wires supplied by Compagnie des Métaux Précieux, Paris. A spectrographic analysis is listed in Table I, which gives a total effective impurity content of about 15 ppm. In the annealed state, the resistivity ratio between room temperature and 4.2 K is 580, after correction for the size effect.

The samples, 12 mm long, were mounted horizontally and soldered at their ends on 1-mm vertical copper wires affixed on a Teflon holder. They were equipped with 0.040-mm-diam potential leads of the same material, spot welded 6 mm apart from each other. This assembly was placed in a vertical pressure vessel, with internal dimensions of 3 cm diam and 12 cm long. The large hydrostatic pressures required were obtained with the help of a standard gas system which enables pressures up to 10 kbar at room temperature and 8 kbar with the vessel immersed in a liquid-nitrogen bath. Helium gas was used as the high-pressure fluid. Pressure was measured with a calibrated manganin gauge.

The annealing was made in situ by direct current heating for 1 h at 1500 °C. When performed in air, this treatment induces an irreversible increase of the base resistance at 273 K of about 6%. This effect is attributed to a reduction of the sample cross section by formation of the oxide PtO_2, which is volatile above 750 °C.[7,8] Consequently all anneals were conducted in a helium atmosphere, under normal pressure. Under these conditions the base resistance is lowered by 2% and the resistivity ratio between 273 K and 4 K is improved by 10%.

Before quenching, the specimens were heated to

TABLE I. Spectrographic analysis of samples: metallic impurities in ppm.

Mg	1	Ni	0.8
Al	0.7	Cu	1
Si	< 3	Rh	1.6
Fe	2	Ir	< 2
Cr	< 0.3	Mn	< 0.2

the desired temperature for a period of 3 min. The heating current of about 9 A was then cut off. A residual current of 0.2 A was kept for the determination of the quench rate. Prior to measurements of the quenched-in resistivity, the gas was evacuated and the lower part of the pressure vessel was disconnected. The specimen holder was then removed and dipped into a helium Dewar for more accurate electrical measurements.

III. EXPERIMENTAL PROBLEMS

It is of primary importance that the quenched-in vacancy concentrations are not disturbed by a possible modification of the vacancy losses during the quench when the quenching conditions are modified. This goal is not easily attained, as the quench rate depends on the pressure, due to slight variations of the thermal conductivity of helium in the pressure range investigated. Emrick[4] attempted to take into account vacancy losses by use of an extrapolation to infinite quenching rate from various linear quenching rates. The actual quenching rates were below 10 000 °C/sec. As far as we are concerned we managed to get high and rather constant rates of (70 000 ± 10 000) °C/sec. For the lower pressures, this result was achieved by immersing the pressure cell in a liquid-nitrogen bath and quenching down to 78 K. For pressures above 1 kbar, for which the rates are high and do not vary much with pressure, the chamber is kept at room temperature.

Another important problem was that of rapid fluctuations of the mean quenching temperature due to convection currents in the gas. This phenomenon was followed by recording the specimen voltage on an oscilloscope. It could be minimized by a maximum filling of the experimental chamber with an aluminium lump. This led to a thermal stability of 2 or 3 °C for wires heated at 1200 °C under 5 kbar. In addition, a special temperature controller was designed, which reduced fluctuations below 0.1 °C, due to the fast response of the electronic system. A check on the longitudinal temperature homogeneity was made using a gold wire with a similar sample geometry. Gold was used since resistance versus pressure and temperature calibration curves are available at elevated temperature and pressure. It was found that at a pressure of 5 kbar the sample could be heated up to within 10 °C of the melting point without indication of melting.

Finally, our greatest concern was to ensure the precise determination of the quench temperature. As is general, this temperature was derived from the resistance of the specimen. At atmospheric pressure, we have used the data issued in Ref. 9. For temperatures ranging between 600 and 800 °C, they can be expressed by

$$\frac{R(t, p_{\text{atm}})}{R(0\,^\circ\text{C}, P_{\text{atm}})} = 1 + 0.3980 \times 10^{-2} t - 0.586 \times 10^{-6} t^2 ,$$

where t is the Celsius temperature.

A special calibration was essential for the high-pressure work, since no high-temperature-high-pressure resistance data were available for Pt. For this purpose a new pressure cell was built consisting of a horizontal tube which was heated by means of an external furnace. The longitudinal gradient in this facility has a parabolic shape, with a temperature difference of 0.5° between the center and positions 1 cm apart from it. The wire specimen was placed along the horizontal axis after bending to a U shape to get a higher compactness; a chromel-alumel thermocouple was placed in a symmetrical position. Data have been collected on thermal cycling between 500 and 700 °C for pressures up to 8 kbar. They are reported in Table II and Fig. 1 together with the values obtained by Bridgman[10] at 0 and 100 °C.

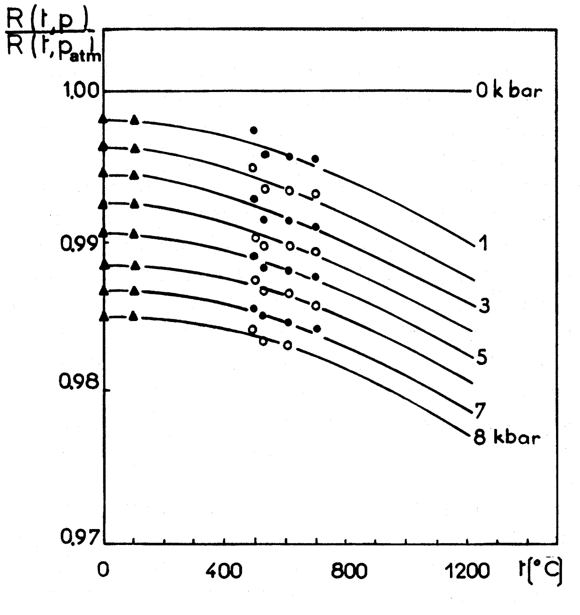

FIG. 1. Influence of pressure on the electrical resistance of platinum: ▲ Bridgman (Ref. 10); ● this work.

TABLE II. Influence of pressure on the electrical resistance of platinum at various temperatures in terms of $R(T,p)/R(T,p_{atm})$.

p(kbar) \ T(°C)	0[a]	100[a]	500	520	600	700
1	0.99803	0.99811	0.9976	0.9955	0.9953	0.9954
2	0.99608	0.99622	0.9950	0.9932	0.9931	0.9930
3	0.99415	0.99435	0.9929	0.9913	0.9913	0.9909
4	0.99224	0.99249	0.9899	0.9896	0.9897	0.9892
5	0.99034	0.99064	0.9889	0.9881	0.9881	0.9876
6	0.98846	0.98879	0.9872	0.9865	0.9865	0.9859
7	0.98660	0.98696	0.9854	0.9850	0.9846	0.9843
8	0.98476	0.98513	0.9843	0.9834	0.9833	

[a] Values obtained by Bridgman (Ref. 10).

IV. VACANCY FORMATION UNDER NORMAL PRESSURE

To validate the quenching and measuring techniques used we first remeasured the formation enthalpy of vacancies in platinum, for low quenching temperatures, using static quenches and helium gas under 2 bar as a cooling medium. The initial quenching rates were about 25 000 °C/sec. Results are shown in Fig. 2, together with those of Jackson.[11] For quenches between 700 and 1000 °C, we obtained a formation enthalpy of 1.47 ± 0.03 eV. This is to be compared to Jackson's value, 1.51 ± 0.04 eV, deduced from immersion quenches in the same temperature range. The agreement is satisfactory, although the quenched-in resistivities differ by a factor of 1.6. Different sink concentrations or quench rates could cause this difference.

V. VACANCY FORMATION UNDER HIGH PRESSURE

A quench temperature of 800 °C was selected. It is close to the maximum temperature at which resistance calibration curves were obtained, so that it can be determined with a good accuracy. Furthermore, the corresponding equilibrium vacancy concentration is about 4×10^{-7} atomic fraction; thus the vacancy interactions during the quench should be negligible under these conditions. After each quench, specimens were annealed directly at 650 °C for 20 min to eliminate the quenched-in defects. This procedure is effective in obtaining a reproducible base resistance. Its variations between two successive quenches were less than 0.5 $\mu\Omega$, when the total quenched-in resistivity was 60 $\mu\Omega$.

Curve 1 on Fig. 3 shows the variation of the quench-induced resistivity increment as measured at liquid-helium temperatures as a function of pressure in the range 0.5–9 kbar. The experimental points for two different samples fit well on a straight line whose slope leads to a value of

$$V^F_{v,800\,°C} = (0.67 \pm 0.03)\, v_{at.,800\,°C} .$$

$v_{at.}$ is the atomic volume at the subscript temperature.

The associated macroscopic relaxation volume per vacancy is given by $V^R = V^F - v_{at.}$, so that

$$V^R_{800\,°C} = -0.33\, v_{at.,800\,°C} .$$

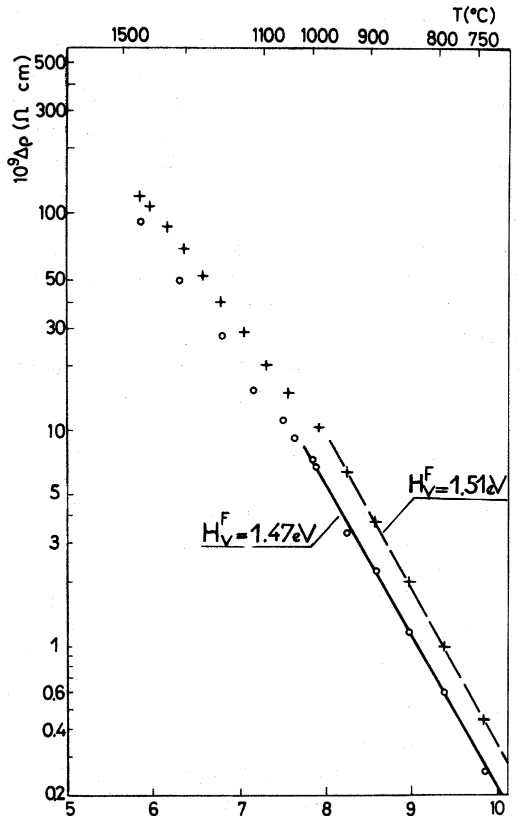

FIG. 2. Resistivity increments in platinum for quenches under normal pressure: + Jackson (Ref. 11); o this work.

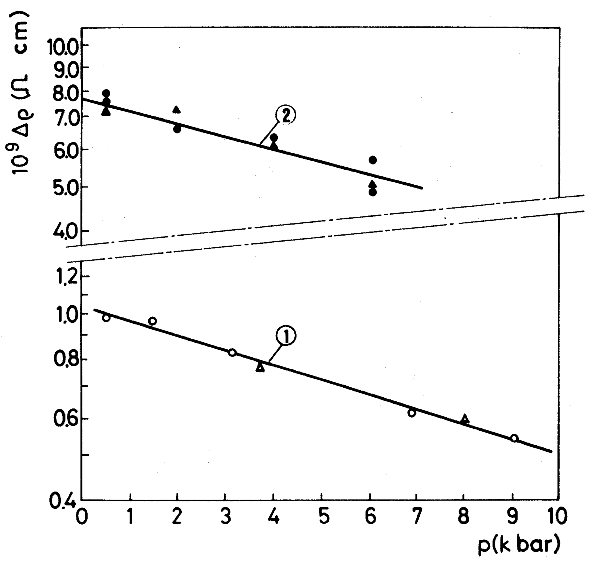

FIG. 3. Resistivity increments in platinum for high-pressure quenches: 1, this work ($T_q = 800\,^\circ\mathrm{C}$); 2, Emrick (Ref. 5) ($T_q = 1060\,^\circ\mathrm{C}$). The symbols ○, △ refer to two different specimens.

If we define a local relaxation volume v^r as the dilatation of a surface surrounding the defect in an infinite medium, the theory of elasticity, as applied to point defects by Eshelby,[12] gives

$$v^r = \tfrac{1}{3}\left[(1+\sigma)/(1-\sigma)\right] V^R \quad ,$$

where σ is the Poisson coefficient of the metal under consideration. For platinum, where σ is 0.39, the local relaxation volume is found to be $-0.25 v_{\mathrm{at.}}$. Hence the inward displacement of first neighbors is 9% of the interatomic distance. It is about two times smaller than for gold.[1-3]

VI. OTHER VALUES OF FORMATION VOLUME

To the authors' knowledge, no theoretical evaluation of the lattice relaxation around a vacant site in platinum is available. This lack is undoubtedly connected with the complexity of the electronic structure of this metal, which makes potential calculations rather difficult. By contrast, a number of efforts have been developed towards the experimental determination of the formation volume. We will now reanalyze and discuss the published results.

A. Lattice-parameter measurements

A significant lattice-parameter decrease has been found recently by Hertz *et al.*[6] in platinum quenched under normal pressure, which gives direct evidence of a lattice contraction due to the presence of vacancies. From the observed proportionality between that parameter decrease and the quenched-in resistivity, using a resistivity of $(5.75 \pm 0.3) \times 10^{-4}$ Ω cm per unit concentration of vacancies,[14] Hertz derives a formation volume of

$$V_v^F = (0.58 \pm 0.06) v_{\mathrm{at.},\,20\,^\circ\mathrm{C}} \;.$$

B. Quenches under pressure

An attempt to quench platinum specimens using a solid pressure-transmitting and cooling medium has been presented recently.[5] The cooling rates of the specimen wires were about 1×10^5 °C/sec. From the comparison of the resistivity increments associated with quenches from 1100 °C under two pressures, namely 0 and 30 kbar, a value of

$$V^F_{v,1100\,^\circ\mathrm{C}} = (0.76 \pm 0.09) v_{\mathrm{at.},\,1100\,^\circ\mathrm{C}}$$

was derived for the formation volume of vacancies.

On another hand, a detailed study of the formation characteristics of vacancies under high pressure has been conducted in platinum by Emrick,[4] with use of the same type of technique which we have employed. The specimen 0.075-mm wires were quenched from temperatures ranging between 1010 and 1200 °C under argon pressures up to 6 kbar. The measured formation volume at these temperatures is

$$V_v^F = (0.70 \pm 0.08) v_{\mathrm{at.},\,20\,^\circ\mathrm{C}} \quad ,$$

as given in Ref. 4. This result is, in fact, the "best" value derived from several values obtained each for a different specimen.[4] It must be noted that quenching rates kept below 10 000 °C/sec. To solve the problem of vacancy losses during the quench, Emrick varied the quenching rate between 300 and 10 000 °C/sec, for a given temperature and and a given pressure, and made a linear extrapolation to infinite quenching rate. The uncertainty resulting from this extrapolation limits the accuracy of the determination. Curve 2 on Fig. 3 is an example of the pressure dependence of such intercepts for two different specimens.

VII. DISCUSSION

Table III summarizes the main results. The uncorrected values show fairly good agreement. In fact, this agreement is coincidental, since a series of important correction factors have not been taken into account. We shall evaluate and discuss now the appropriate corrections to be made for a valid comparison.

The first one deals with the definition of the quench temperature and applies only to the high-pressure work. In Emrick's[4] investigation, it has been determined from Bridgman's calibration at 100 °C of resistance versus pressure. Thus the temperature scale is in error at the elevated temperatures from which quenches are made. We

TABLE III. Formation volume of vacancies in platinum, in fractions of atomic volume. All the results have been normalized with respect to the atomic volume at 20 °C.

Method	Temperature of determination (°C)	Ref.	Uncorrected value ($v_{\mathrm{at.},T}$)	Correction for temperature calibration ($v_{\mathrm{at.},T}$)	Correction for thermal expansion of the lattice ($v_{\mathrm{at.},20\,°\mathrm{C}}$)	Intrinsic variation of V_v^F by reference to 800 °C	Final value at 800 °C ($v_{\mathrm{at.},20\,°\mathrm{C}}$)
Atm. pressure parameter measurements	20	6	0.58 ± 0.06	0	0	+0.15	0.73 ± 0.06
High-pressure quenches							
gas (Ar)	1100	4	0.67 ± 0.08	+0.13	+0.03	−0.05	0.78 ± 0.08
gas (He)	800	this work	0.67 ± 0.03	0	+0.02	0	0.69 ± 0.03
solid (BN)	1100	5	0.76 ± 0.09	+0.11	+0.03	−0.05	0.85 ± 0.09

have applied to Emrick's results a correction derived from an extrapolation of the calibration data we obtained up to 700 °C (Fig. 1). On this basis, it is found that Emrick's indicated quench temperatures were too high by 7 °C at 1000 °C and by 9 °C at 1200 °C at a pressure of 6 kbar, with an uncertainty of 1°. This induces an average correction on the measured formation volume of +0.13 atomic volume.

In Senoo's work, no correction at all was made for the effect of pressure on the resistance-temperature calibration curve. From our data at 8 kbar, 700 °C, using for temperatures the extrapolation indicated on Fig. 1, and for pressures a linear extrapolation from 8 to 30 kbar that we have verified to be valid from 4 to 8 kbar, we are led to a correction of about 15 °C at 1100 °C. The incident correction for the formation volume at 1100 °C would be +0.11 atomic volume.

A second correction factor affects all the results. Up to recent years, it was usual to consider that the relative temperature dependence of the formation volume of vacancies was identical to that of the volume of the host metal. However, recent experiments in zinc and cadmium[15–17] have shown evidence that, at least in these metals, the self-diffusion volume was more markedly temperature dependent than expected from the ideal-lattice thermal-expansion coefficient, namely,

$$\frac{1}{V^F}\frac{\partial V^F}{\partial T}\bigg|_P \simeq 15\,\frac{1}{V}\frac{\partial V}{\partial T}\bigg|_P .$$

An atomistic calculation based on a Morse-like potential confirmed the experimentally measured order of magnitude of this effect in zinc.[15]

Thus, from the above considerations, we have tentatively taken a value of 5 for the magnification coefficient, to evaluate roughly the variation of the formation volume of vacancies with temperature in platinum. The corresponding corrections are listed in Table III, by reference to a standardization temperature of 800 °C.

To summarize, it appears that the agreement for the corrected values is practically within experimental error. It must, however, be recognized that Senoo's results show considerable scatter as illustrated in Fig. 3. Furthermore, a strong curvature is evident on the Arrhenius plot of the quenched-in resistivity at 30 kbar. Thus experiments under solid pressure must be considered with care, due to experimental problems involved, although they eliminate contamination risks by the quenching medium, at least as far as gases are concerned.

We close by mentioning the possible influence of rare gases on the vacancy's characteristics as determined by high-pressure gas quenches. Evidence for the dissolution of helium and its interaction with lattice vacancies has been shown in quenched gold.[18,19] Its disturbing role on the determination of the formation volume of vacancies has been clearly established for the high quenching temperatures.[19,20] We have, in fact, detected a similar effect in platinum specimens quenched from high temperatures, 1060 and 1200 °C, leading to apparent values largely in excess of the proper formation volume.[13] Further studies are in progress to obtain a better understanding of the role played by dissolved gases in this type of experiment. Their effect on the formation volume measurements should be negligible for the lower quench temperatures.

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