

# Effects of Vacancies on the Physical Properties of Platinum

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Most of those who work with metals at high temperature think of vacancies (vacant lattice sites) as important only in the context of diffusion. It is usually left to the solid-state physicist to study the effects of vacancies on such physical properties as thermal expansion, enthalpy and electrical resistivity, and even he may be interested largely in what he can learn about the vacancies themselves. Of course, whereas diffusion is a process *controlled* by vacancies, vacancies merely *influence* these other properties to a limited extent. Nevertheless, the influence can be sufficient to be of direct concern to those who use platinum as a high-temperature reference material.

## The Size of Vacancy Effects

As is well known, the equilibrium monovacancy concentration  $C(T)$  in a metal is an

exponential function of the absolute temperature  $T$ :

$$C(T) = \exp(S^F/k) \exp(-E^F/kT)$$

where  $C$  is the atomic fraction of vacancies,  $S^F$  is the monovacancy formation entropy,  $E^F$  is the monovacancy formation "energy" (enthalpy), and  $k$  is Boltzmann's constant.

Because of this, at temperatures approaching the melting point  $T_m$  the variation of  $C$  with temperature is so rapid that, although the effect of vacancies on, say, the electrical resistivity may be quite small ( $\approx 1$  per cent), the effect on the corresponding *differential* property—the temperature coefficient of resistivity—is an order of magnitude larger at least.

To make precise estimates of vacancy effects in platinum is not altogether easy. The "traditional" experiment (1) of accurately

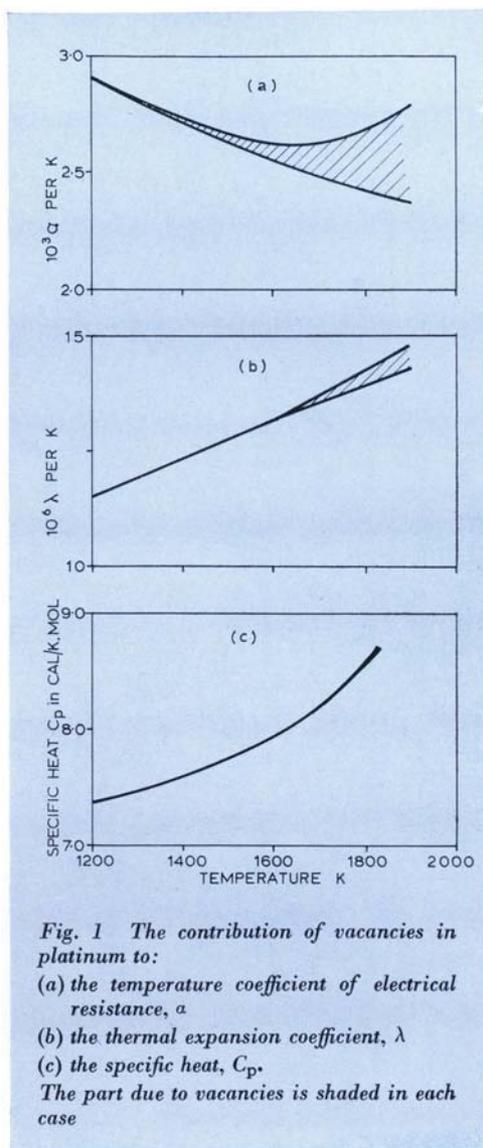
The Effect of Vacancies on Some Physical Properties of Pure Platinum. Creation of Vacancies as the Temperature Rises Makes the Indicated Percentage Contributions to the Properties Shown			
Temperature K	Temperature Coefficient of Electrical Resistance	Coefficient of Linear Thermal Expansion	Specific Heat
1450	2%		
1550	3%		
1650	4½%	1%	
1750	8%	2%	
1850	13%	3½%	½%
1950	23%	6%	1%

comparing specimen length and X-ray parameter to give vacancy concentration is difficult at the high temperatures involved. Diffusion studies are complicated by the tendency of monovacancies at high concentration to aggregate into divacancies, and quenching studies are difficult to relate to the high-temperature near-equilibrium situation. A combination of techniques is necessary to arrive at a set of self-consistent vacancy parameters (2).  $S^F/k=1.3$  and  $E^F=1.49$  eV are accepted values, giving  $C(T_m)=8 \times 10^{-4}$ . Using these with other data, we can estimate the effect of vacancies on some physical properties to be as shown in the Table; the large effect on the temperature coefficient of electrical resistance is evident.

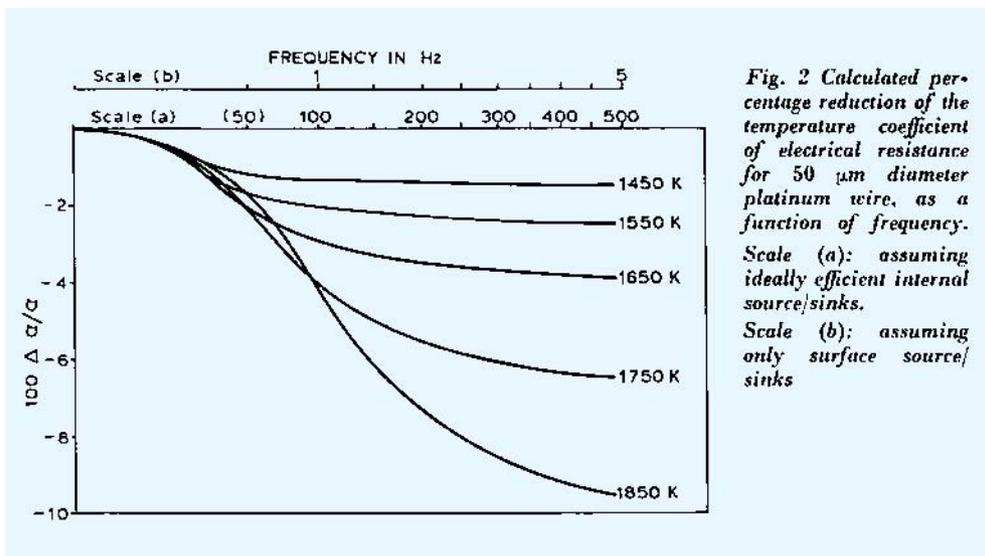
Until quite recently, controversy existed (3, 4) as to whether these estimates were correct, as a different procedure was in use which gave the vacancy concentration to be an order of magnitude higher. In this procedure the values measured for a physical property below about 1400K were extrapolated to higher temperatures and taken to define the "background" values appropriate to an ideal vacancy-free metal. Subtraction from the observed high-temperature values then gave an estimate of the vacancy effect. Thus for platinum the observed sharp rise of the specific heat vs. temperature curve was used (5) to estimate  $C(T_m)$  to be as high as 1 per cent. This estimate is now known to be too large (2, 6). Much of the difference between the extrapolated and experimental curves is now attributed to anharmonic interatomic forces, so that the true background cannot be found by simple extrapolation (7) (Fig. 1); an additional complication in determining the background is the temperature variation of the electronic specific heat.

### Transient Effects of Vacancies

Vacancy effects, then, are only part of the reason why values of physical properties measured above  $2/3 T_m$  differ from those measured below that temperature. But



vacancy effects are different from the rest in that they alone can give rise to time delays in the measured properties at high temperatures; this is because the vacancy concentration takes a measurable time to adjust to a change of temperature. Vacancies have to be created at definite sources or destroyed at definite sinks, so that diffusion of vacancies must take place before the vacancy concentration everywhere relaxes to the value appropriate to the new temperature.



*Fig. 2 Calculated percentage reduction of the temperature coefficient of electrical resistance for 50  $\mu\text{m}$  diameter platinum wire, as a function of frequency.*

*Scale (a): assuming ideally efficient internal source/sinks.*

*Scale (b): assuming only surface source/sinks*

All vacancy-affected physical properties will similarly take this time to reach their final values.

Instead of concentrating on time-delay behaviour, we may regard these properties as frequency-dependent (8) (just as simple dielectric relaxation may be expressed as a Debye spectrum). The detailed frequency dependence is determined by the vacancy diffusion coefficient, the source/sink geometry, and the source/sink efficiency. We must therefore expect the frequency dependence to be influenced by temperature (via the vacancy diffusion coefficient,  $D$ , at least).

The sources and sinks for vacancies above  $\frac{2}{3} T_m$  cannot be identified certainly; it is not safe to assume, say, that sinks identified in an annealing experiment below  $\frac{1}{3} T_m$  will operate at the higher temperature. However, Heigl and Sizmann (9) have studied the generation of vacancies in platinum wires pulse-heated to temperatures up to  $\approx 1200\text{K}$  for times ranging from  $\approx 1$  ms. From a detailed study of the kinetics, they concluded that the vacancy sources were quasi-planar, with a spacing put at  $\approx 5 \mu\text{m}$ ; the sources were thus presumed to be dislocations in low-angle sub-grain boundaries.

Assuming this geometry, and that these sources function with ideal efficiency as source/sinks (so that at the boundaries the vacancy concentration is always at the equilibrium value appropriate to the instantaneous temperature), we can calculate (10) the frequency dependence of, say, the temperature coefficient of resistance for small temperature changes about a given mean temperature. This is shown in Fig. 2a. Although the curves look superficially like Debye relaxation curves, they cannot strictly be described by a single relaxation time, even for a given mean temperature: at high frequencies, the variation depends on  $\omega^{-\frac{1}{2}}$  (and not the Debye  $\omega^{-1}$ ). This is because only the region of the sub-grain within a distance  $(D/\omega)^{\frac{1}{2}}$  of the boundary can participate in the changes in vacancy concentration.

The time scale for vacancy relaxation effects calculated in this way is very much a lower limit: if, for any reason, the internal source/sinks should function with less than ideal efficiency, then the time scale will be longer. As an upper limit, we may take the surface of the specimen to be the only source/sink, and, for example, calculate that for wires of  $50 \mu\text{m}$  diameter the time scale is

increased by a factor of 100 (Fig. 2b) compared with that for internal source/sinks.

## The Practical Importance of Vacancy Effects

The most important factor in determining the efficiency of the internal source/sinks is the vacancy subsaturation (or supersaturation), which provides the forces causing the dislocation to climb, with emission (or absorption) of vacancies (12). In pure platinum, temperature changes of only a few kelvin should be sufficient to cause the internal source/sinks to operate. The time scale of vacancy relaxation effects will then approximate to Fig. 2a, too short to be of interest in conventional potentiometry. However, for temperature transients in electrically heated wires and foils, the time scale can become significant.

Temperature modulation experiments combine the short time scale with the accuracy needed to observe these effects. A.C. heating is used to cause in a hot wire specimen a near-sinusoidal temperature variation of, say,  $\pm 1\text{K}$  at 30Hz. For platinum the temperature variation may conveniently be measured by using the variation in light emitted. The measured variation in electrical resistance then gives the temperature coefficient of resistivity appropriate to the modulation frequency. At 1850K and 30Hz, this coefficient is found to be some 5 to 10 per cent below the quasi-static value, confirming a vacancy relaxation effect (6). The accuracy of the measurements is not sufficient to determine exact vacancy kinetics and source/sink efficiency though the efficiency is clearly less than ideal. But already it is clear that to neglect the frequency dependence of the temperature coefficient of resistance will cause significant systematic error in experiments in which resistance changes during thermal transients are used to measure the temperature changes involved. Systematic errors of this kind inflate specific heat values (5) and thermal expansion coefficient values

(13) reported from modulation experiments in which quasi-static values of temperature coefficient of resistance were (erroneously) used throughout.

The situation in impure platinum is less clear. Impurities may be expected to decrease the efficiency of the internal source/sinks, and effects of this have been reported in other metals (14), where the time scale of events became the time needed for vacancies to diffuse from the surface into the bulk. Similar effects in impure platinum, or platinum alloys, could possibly influence conventional potentiometric measurements. However, the impurities in platinum are often of the platinum group of elements, and these might have little effect on the internal source/sinks.

Further work on this problem is to be undertaken at the City University with the cooperation of Johnson Matthey and Co Limited.

## References

- 1 R. O. Simmons and R. W. Balluffi, *Phys. Rev.*, 1960, **119**, 600
- 2 D. Schumacher, A. Seeger and O. Harlin, *Phys. Stat. Solidi*, 1968, **25**, 359
- 3 Ya. A. Kraftmakher and P. G. Strelkov, "Vacancies and Interstitials in Metals", North Holland, 1970, p. 59
- 4 M. Hoch, *Ibid.*, p. 81
- 5 Ya. A. Kraftmakher and E. B. Lanina, *Fiz. Tverd. Tela*, 1965, **7**, 123
- 6 A. H. Seville, *Phys. Stat. Solidi A, Appl. Res.*, 1974, **21**, 649
- 7 A. H. Seville, *J. Chem. Thermodynamics*, 1975 **7**, 383
- 8 J. Van den Sype, *Phys. Stat. Solidi*, 1970, **39**, 659
- 9 F. Heigl and R. Sizmann, *Crystal Lattice Defects*, 1972, **3**, 13
- 10 A. H. Seville, Ph.D. Thesis, University of Edinburgh, 1972, p. 30
- 11 V. E. Zinoviev, I. G. Korshunov and P. V. Geld, *Fiz. Tverd. Tela*, 1971, **13**, 3459
- 12 V. M. Lomer, "Vacancies and Other Point Defects in Metals and Alloys", Institute of Physics Monograph and Report Series No. 23, 1958, p. 94
- 13 Ya. A. Kraftmakher and I. M. Cheremisina, *Zh. Prikl. Mekh. Tekh. Fiz.*, 1965, **2**, 114
- 14 B. S. Bokstein, S. Z. Bokstein, A. A. Zhukovitskii, S. I. Kishkin, L. G. Kornelyuk and Yu. S. Nechaev, *Dokl. Akad. Nauk S.S.S.R.*, 1968, **183**, 1280