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Unit-cell dimensions of Ni-Pd alloys at 25 and 900 °C.*

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The present lattice parameter studies were undertaken in conjunction with an investigation of the thermodynamic properties of Ni–Pd alloys at elevated temperatures (Bidwell & Speiser, 1964). The primary purpose was to provide an independent check of the published room temperature data, which contain conflicts, and to define the volume properties of the alloys in the same temperature region in which the other thermodynamic properties were being investigated.

Hultgren & Zapffe (1939) determined the room temperature cell constants of well homogenized Ni–Pd alloys that had been annealed for long periods at 600 and 400 °C. They concluded that there were no ordering reactions in the system and failed to find a miscibility gap suggested by Fraenkel & Stern (1927). Their cell constants followed a smooth curve as a function of composition with a considerable positive deviation from Vegard's law (Fig. 1). Kondrashev, Tverdovski & Vert (1951) measured the lattice constants of alloys prepared by the electrolysis of complex salt baths and obtained an irregularly shaped curve showing a considerable deviation from Hultgren & Zapffe's data in the regions 10–30 and 70–100 at.% Pd (Fig. 1). They admitted, however, that these anomalies might be associated with the method of alloy preparation. Recently, Nosé (1961), investigating alloy thin films prepared for magnetic studies, obtained cell constants agreeing roughly with those of Hultgren but showing considerable scatter, particularly in the same composition ranges where Kondrashev *et al.* obtained their anomalous results.

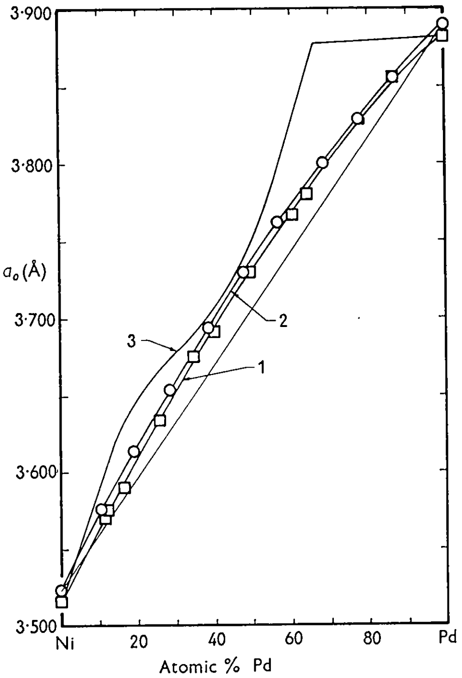

Fig. 1. Comparison of unit-cell dimensions of Ni–Pd alloys at ambient temperature. 1. Hultgren & Zapffe (1939). 2. This investigation. 3. Kondrashev, Tverdovski & Vert (1951).

In this investigation the cell constants were measured at 25 and 900 °C with a Unicam, 19 cm, high-temperature X-ray powder camera using Cu $K\alpha$ radiation. Specimen temperatures were measured with a Pt–13% Rh thermocouple calibrated *in situ* against the body-centered cubic to face-centered cubic transformation of high-purity zone-refined iron. The temperature of this transformation was assumed to be 910 °C. Specimen temperatures were maintained constant to within ±1·5 °C by a constant voltage power supply.

The alloys were prepared from high-purity nickel and palladium by induction melting in vacuum. The details of the preparation and treatment are described elsewhere (Bidwell & Speiser, 1964). The final purity for all alloys was greater than 99·97%. The major impurities, in decreasing order of importance were: Rh, Fe, Pt, Si, and C, all of which occurred in quantities less than 60 ppm. Powder specimens were removed from the alloy ingots by grinding with a tungsten carbide dental drill. The powder was sealed in evacuated thin-walled fused silica capillary tubes and annealed in the camera at 1000 °C for one-half hour. After annealing, diffraction photographs were taken at 900 °C and 25 °C. Cell constants were determined from the experimental data by the method of Nelson & Riley (1945).

The cell constants obtained for the alloys at 25 and 900 °C are listed in Table 1. The precision of these values is estimated to be ±1 part in 10,000 for the 25 °C measurements and ±3 parts in 10,000 for the 900 °C measurements. The 25 °C cell constants of 3·523 (5) and 3·890 (0) Å obtained for pure nickel and palladium respectively, compare favorably with the values 3·5238 and 3·8898 Å determined by Swanson & Tatge (1951, 1953). In view of the excellent agreement with the

Table 1. *Cell constants and molar volumes of* Ni–Pd *alloys at 25 and* 900 °C

	25 °C			900 °C		
At.% Pd	a_0 (Å)	V (cm^3.mol^{-1})	ΔV^M (cm^3.mol^{-1})	a_0 (Å)	V (cm^3.mol^{-1})	ΔV^M (cm^3.mol^{-1})
Ni	3·523(5)	6·59		3·575(7)	6·88	
10·7	3·575(3)	6·88	0·051	3·628(9)	7·20	0·065
19·1	3·613(1)	7·10	0·080	3·665(7)	7·42	0·091
28·7	3·654(1)	7·35	0·105	3·707(6)	7·67	0·127
38·2	3·693(6)	7·59	0·130	3·747(4)	7·92	0·158
47·4	3·730(5)	7·82	0·151	3·783(5)	8·15	0·176
56·4	3·762(6)	8·02	0·150	3·814(4)	8·36	0·170
68·1	3·799(6)	8·26	0·123	3·849(8)	8·59	0·134
77·7	3·828(5)	8·45	0·093	3·879(0)	8·79	0·109
86·5	3·855(5)	8·63	0·074	3·904(5)	8·96	0·081
Pd	3·890(0)	8·86		3·937(8)	9·19	

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* The experimental work was conducted at ARL.

data published for the pure metals, calibration of the X-ray camera for the measurements on the alloys was not considered necessary.

The room temperature lattice constants obtained by Hultgren & Zapffe and by Kondrashev *et al.* are compared with the values obtained in this investigation in Fig. 1. The data of this investigation are in excellent agreement with those obtained by Hultgren & Zapffe. In contrast to the observations of Kondrashev *et al.*, whose alloys were obviously not in equilibrium, the cell constants follow a smooth curve with a considerable positive deviation from Vegard's law. The molar volumes (V) and the relative integral molar volumes (ΔV^M, volumes of mixing), calculated from the relation

$$\Delta V^M = V - (N_{\text{Ni}} V^0{}_{\text{Ni}} + N_{\text{Pd}} V^0{}_{\text{Pd}}) \,,$$

where N_i and V_i^0 are respectively the mole fraction and molar volume of pure component i, are also shown in Table 1. In many respects the volume of mixing presents a more realistic picture of the effects of alloying than do the cell constants, since a solution which obeys Vegard's law represents a negative deviation from the rule of mixtures in a volume sense.

In view of the recent suggestions, *e.g.* Myalikgulyev (1959) and Permanova (1961), that a superstructure exists at about 75 at.% Pd, the cell constants of the 77·7 at.% Pd alloy were determined as a function of time at 700 (7 days) and 510 °C (14 days). It was expected that if the system tended toward long-range order, the ordering reaction would be accompanied by an increase in volume as in the similar Fe–Pd system which forms a superlattice below 800 °C (Hultgren & Zapffe, 1939). However, within the precision of the measurements, the cell dimensions remained constant at 3·868 (0) and 3·858 (4) Å respectively.

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Solution of the phase equations representing non-crystallographic symmetry.

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A set of phase relationships must be satisfied whenever the asymmetric unit contains some non-crystallographic symmetry. For instance if there are two molecules or subunits in the asymmetric unit which are related by a local twofold axis, as is the case for α-chymotrypsin (Blow, Rossmann & Jeffery, 1964), there are conditions which the phase angles must fulfill if the electron density distributions of the two subunits are to be equal. The derivation of the necessary conditions has been given by Rossmann & Blow (1963) (equations (7) and (8)). These two equations may be combined to give an equation of the form

$$\sum_j A_{ij} \exp\,[i(\alpha_i + \alpha_j + \varphi_{ij})] = S_i \tag{1}$$

for each reflection. Here i and j identify the individual reflections, and the quantities A_{ij}, S_i and φ_{ij} can be calculated from a knowledge of the structure amplitudes and the rotational and translational relationship between the two independent molecules. α_i and α_j are the phases of the ith and jth structure factor. In any one equation there are few terms with significantly large magnitudes A_{ij}.

Since writing the previous paper (Rossmann & Blow, 1963) we have found an alternative procedure leading towards a solution of these equations which we believe to be superior, as it considers the interdependence of each of the terms in a single equation instead of treating them independently. Also, the amount of computation involved is greatly reduced.

Let us write (1) as

$$\exp\,(i\alpha_i) \sum_j A_{ij} \exp\,[i(\alpha_j + \varphi_{ij})] = S_i \tag{2}$$

or

$$T_i \exp\,[i(\alpha_i + \Phi_i)] + A_{ii} \exp i(2\alpha_i + \varphi_{ii}) = S_i \tag{3}$$

where

$$T_i \exp\,(i\Phi_i) = \sum_{j \neq i} A_{ij} \exp\,[i(\alpha_j + \varphi_{ij})] \,. \tag{4}$$

At any stage of the refinement we have an estimate of the phase angle α_i from previous results. The precision of this estimate can be expressed in terms of a figure of merit m_j (Dickerson, Kendrew & Strandberg, 1961) which varies from unity for complete certainty about the phase angle to zero when there is no phase information. We propose to replace (4) by the following expression for actual calculation: