Estimating volume fractions of superabundant vacancy phases and their potential roles in low energy nuclear reactions and high conductivity in the palladium – isotopic hydrogen system

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\section*{1. Introduction}

Superabundant vacancies (SAV) in face centered cubic (FCC) metals change the unit cells from FCC to simple cubic (SC) with vacancies (Vac) replacing all 8 corner atoms of the FCC unit cell, creating long strings of Vac that intersect at the corners of unit cells in three orthogonal directions [1]. This Vac ordering is similar to the gold (Au) strings of Vac that intersect at the corners of unit cells in three orthogonal directions. In palladium (Pd), ordered SAV structures are: Pd\textsubscript{3}Vac\textsubscript{D}\textsubscript{4} (δ or δ′ phases) [2–6] where x is between 4 and 8, and Pd\textsubscript{7}Vac\textsubscript{D}\textsubscript{6–8} (γ phase) [7]. Isotopic hydrogen (protium (H), deuterium (D), or tritium (T)) occupy octahedral interstitial sites (δ phase, Pd\textsubscript{3}Vac\textsubscript{D}\textsubscript{4}) [2–4] and/or occupy tetrahedral interstitial sites (δ′ phase, Pd\textsubscript{7}Vac\textsubscript{D}\textsubscript{6–8}) [5,6].

SAV phases result from hydrogen-induced vacancy formation [2–4,7–25]. It has been shown [1,26] that creation of SAV structures near room temperature requires creation of vacancies by a mechanism other than diffusion (dragging of jogs by screw dislocations) and re-location of vacancies (attraction to electromigrating D\textsuperscript{+} ions). Vac have higher mobility (validated by density functional perturbation theory (DFT) [12,19–25]) from being dragged by electromigrating D\textsuperscript{+} ions (charge is not necessarily equal to +1.0, but might be a partial positive net charge) to form SAV structures [1,26] and higher numbers of Vac are promoted by high dislocation density [1,26] and the mechanism presented in Appendix B of [1]. The kinetics of these two steps in the formation of room temperature SAV make SAV possible under room temperature electrolysis where conventional diffusion kinetics are too slow. Even so, the nucleation and growth of δ and δ′ to large volume fractions in the bulk quickly by this two-step mechanism are not anticipated because of a limited supply of vacancies and low kinetic rates. The SAV phase, supporting excess heat, can be shown to be a small volume fraction [1]. The limited rate of creation and ordering of vacancies at room temperature explains the incubation period to initiate...
excess heat in many low energy nuclear reaction (LENR) experiments [1,26].

Fig. 1 shows the proposed equilibrium phase diagram of palladium – isotopic hydrogen [1,26] with δ and δ′ phases centered near D/Pd = 1.33 while δ′ extends to 2.66: details of its development are reported elsewhere [1]. The δ′ appears below a temperature of 375 °K based on resistivity data [1] and is supported by measured tetrahedral occupancy by D from Pitt and Gray [5] and Ferguson et al. [6]. From DFT, Isaeva et al. [19] found, at lower temperatures, occupancy of tetrahedral sites by D stabilizes SAV more than at octahedral sites. Neutron diffraction data by two research groups [5,6] show D (H) migrates from octahedral to tetrahedral sites at lower temperatures. There are twice as many interstitial sites in δ′ as in δ. The δ and δ′ phases are of interest to the study of LENR and high electrical conductivity, respectively. The lower isotopic hydrogen composition phases of metal hydrides (α and β) have ordinary structures and electron distributions and might not be capable of supporting high conductivity and nuclear reactions. However, SAV phases of δ, and δ′ have open tubes or channels (intersecting strings of vacancies) [1] for fast transport conditions, unfamiliar electron–proton (or deuteron) interaction, and are insufficiently studied. The purpose of this investigation is to estimate their volume fractions and posit the nature and roles each phase plays.

2. Materials and methods

The experimental materials and methods are detailed in an earlier work [1] including electromigration in Appendix A of that study. The electrolytic cells, with Pd/D2O and with Pt/H2O [1], are shown in Fig. 2 with the important features of ability to measure resistivity in situ as well as determine excess heat (more energy out than put in). Resistance measurements verified loading of Pd over the resistive hump at D/Pd = 1.33 while δ′ extends to 2.66: details of its development are reported elsewhere [1]. The δ′ appears below a temperature of 375 °K based on resistivity data [1] and is supported by measured tetrahedral occupancy by D from Pitt and Gray [5] and Ferguson et al. [6]. From DFT, Isaeva et al. [19] found, at lower temperatures, occupancy of tetrahedral sites by D stabilizes SAV more than at octahedral sites. Neutron diffraction data by two research groups [5,6] show D (H) migrates from octahedral to tetrahedral sites at lower temperatures. There are twice as many interstitial sites in δ′ as in δ. The δ and δ′ phases are of interest to the study of LENR and high electrical conductivity, respectively. The lower isotopic hydrogen composition phases of metal hydrides (α and β) have ordinary structures and electron distributions and might not be capable of supporting high conductivity and nuclear reactions. However, SAV phases of δ, and δ′ have open tubes or channels (intersecting strings of vacancies) [1] for fast transport conditions, unfamiliar electron–proton (or deuteron) interaction, and are insufficiently studied. The purpose of this investigation is to estimate their volume fractions and posit the nature and roles each phase plays.

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3. Analysis and results

The following analysis uses the production of nuclear energy from the arrangement in Fig. 2, and significant changes in resistivity of the Pd-D, to estimate the volume fractions of δ, and δ′ phases, respectively. The development of the concentration profile of ionic interstitials of D⁺ is shown in Fig. 3 with further details in Appendix A of reference [1]. The ratio of concentration at the right end of the Pd wire compared to the left end, D/Pd enhancement, is also in Table 1 as CL/CO. For conditions of 0.05 cm diameter and ~1.5 A, theoretical enhancement is about 2 times (or slightly less, CL/CO = 1.38, if Z = 0.4, see Table 1 footnote).

This does not include any contribution from electrolysis current (Fig. 2). ELECTROLYSIS current also contributes to electromigration and enhancement. The Appendix A (below) shows the method of incorporating this effect. It can, conservatively, be ignored when

Fig. 1. Equilibrium Phase Diagram for Isotopic Hydrogen – Palladium after reference [1] with modified phase field near higher compositions of δ′: there can be as many as 8 tetrahedral D atoms per unit cell in δ′ but only 4 octahedral D atoms per unit cell in δ. At higher D/Pd ratios D fills these extra sites making δ′ a more stable (lower free energy) phase at these compositions.

Fig. 2. Electrolytic cells of four nested (not shown) Pyrex test tubes with Pd or Pt cathodes and Pt anodes, sealed with Teflon tops (not shown). Both cells are in series on one “current controlled” power supply (P.S.). Independent electromigration currents from P. S.’s for each cell were also operated in “current control” mode, from [1].

Fig. 3. Pd between two Cu leads, the two fluxes that develop and the resulting concentration profile.

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Using the law of mixtures, the sum of the resistivity of δ′ phase, times its volume fraction (fv(δ′)), and ρβ on the curve of Fig. 5 which are all solutions satisfying the rule of mixtures to bring down overall resistivity to the measured value, but the solution with ρβ = 0 is the most likely, as discussed below. If ρβ is 0, the real volume fraction for δ′ phase, fδ′(δ') (not 0.03%, but low), can be determined. Using the law of mixtures, and solving for fδ′(δ') gives fδ′(δ') = 1 - ρbulk/ρβ = 1 - (17.61·10^{-6} - 0.946·10^{-6})/17.61·10^{-6} = 0.51% (Fig. 4a) and = 5.0% (Fig. 4b, with 17.63·10^{-6}), considerably higher than the volume fraction for δ.

4. Discussion

If other conditions (Fig. 5) are invoked for volume fractions calculation, it becomes higher than fδ′(δ') ≈ 5%. These are less probable due to the inference that fδ′(δ') should be near fδ(δ), since they should share the same rα, and both result from hydrogen-induced vacancy formation and the same atomic arrangement except for location of D atoms. More importantly, kinetics for formation of SAV (Vac number and Vac mobility) will limit volume fraction to the lowest value satisfying the rule of mixtures (Fig. 5, fδ′(δ') ≈ 5%). Limited supply of D also discourages large fδ′(δ'). With δ′ having twice the number of interstitial sites than δ

ΔVmin = 0.0378 V. The constant electromigration current I for the first specimen (Fig. 4a) was 1.235 A, and for the second specimen (Fig. 4b) was 1.422 A. Electrosorption current iS should be included when considering these voltage drops. The Appendix A shows the appropriate value of electromigration current to be added to electromigration current I is one half of its value, for a total of (1 + iS/2).

Thus ρS/ρPd = 1.718 at rα = 0.93 which is rα measured before the resistivity change and therefore, ρPd = 1.718(10·8·10^{-6}) = 18.56·10^{-6} Ω-cm, where ρPd = 10.8·10^{-6} Ω-cm is resistivity of unalloyed Pd [33]. The drop in bulk resistance due to phase change is ΔR = ΔVmax/ΔVmin = (1/422 + 0.471/2) = 0.001224 Ω and (0.0398–0.0378)/(1.422 + 0.471/2) = 0.001207 Ω for Fig. 4a and b, respectively. This corresponds to a change in resistivity due to phase change Δρ = ΔR/ρ = (0.001224)(1.963·10^{-3})/2.54 = 0.946·10^{-6} Ω-cm (Fig. 4a) and = 0.933·10^{-6} Ω-cm (Fig. 4b).

Now that resistivity for multiphase Pd (ρbulk) is determined, resistivity of the individual δ′ phase can be determined using the law of mixtures and the component fraction:

ρbulk = ρδ′(δ′) + ρβ(δ′)

Resistivity of δ′, assuming the same volume fraction as δ, is

ρδ′(δ′) = [ρbulk - ρδ(δ)]/fδ′(δ′) = [ρbulk + ρδ(δ)]/(1-fδ(δ))

= [17.61·10^{-6} - 18.56·10^{-6}]/0.0003 = -0.00314 Ω-cm (Fig. 4a), or = -0.00308 Ω-cm (Fig. 4b with ρbulk = 17.63·10^{-6} Ω-cm). The negative values are not real possibilities (fδ′ cannot be less than zero) and just indicate the value for ρδ′ should be 0, and thus 0.0003 is not the real value of fδ′(δ′). It has to be higher for ρδ′ to be 0. Thus δ′ has zero resistivity if fδ′(δ′) is near fδ(δ). This would suggest it is superconducting. However, there are other possibilities: those combinations fδ(δ) and ρβ on the curve of Fig. 5 which are all solutions satisfying the rule of mixtures to bring down overall resistivity to the measured value, but the solution with ρβ = 0 is the most likely, as discussed below.

If ρβ is 0, the real volume fraction for δ′ phase, fδ′(δ′) (not 0.03%, but low), can be determined. Using the law of mixtures, and solving for fδ′(δ′) gives fδ′(δ′) = 1 - ρbulk/ρβ = 1 - (17.61·10^{-6} - 0.946·10^{-6})/17.61·10^{-6} = 0.51% (Fig. 4a) and = 5.0% (Fig. 4b, with 17.63·10^{-6}), considerably higher than the volume fraction for δ.

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For filling, these should fill more completely rather than create more δ′.

The fact that the average bulk ratio $r_x \approx 1.0$ is less than that required for δ′ ($\geq 1.33$), would also limit $f_v(\delta')$. This value of resistivity ($\rho_{\delta' = 0} = 0$ for $f_v(\delta') = 5\%$) and its implication of superconductivity for δ′, supports suggestions and conclusions of Syed et al. [34], Tripodi et al. [35], Anderson [36] and Sinha [37] and supports increased electron-photon coupling. It would also imply δ′ and δ″ (as well as possibly ε) are one and the same phase (Fig. 1).

This conclusion about the resistivity of δ′ and its volume fraction would mean significant variation in resistivity (0 to 18.56·10−6 Ω-cm) with location in the bulk (δ′ vs β phase) with only a very small additional volume fraction of δ scattered throughout the bulk, producing nuclear energy. This is consistent with observed local hot spots for production of tritium observed by Will et al. [38] and Srinivasan et al. [39]. It is also consistent with small and scarce local explosive reactions in the lattice in near-surface region from volcanic-like eruptions observed in optical and scanning electron microscopy of the surface after excess heat [40].

A drop in resistivity while temperature increases (Fig. 4), is not expected behavior of PdD. Most metals and metal hydrides (or deuterides) show increasing resistivity with temperature [41–43], as in Fig. 6. This behavior strongly suggests that the drop in resistivity is from a phase change. If excess heat is from δ (Pd3VacD4 with D in octahedral sites), then formation of δ′ (Pd3VacD4 with D in tetrahedral sites), (Fig. 7) enables extensive pathways of low resistance for electron transport along vacuum tubes, which are “vacancy channels of undulating diameter”, free of atoms, along all edges of unit cells. The only nearest Pd neighbors are face-centered atoms (see Figs. 7 or 8) along close-packed directions $\langle 1 1 0 \rangle$ (Pd atom diameters $d_{\text{Pd atom}}$ have zero separating distance along $\langle 1 1 0 \rangle$). This leaves the minimum opening or diameter of the tube in Fig. 8 (considering only Pd atoms) at 1.4142·$d_{\text{Pd atom}}$ – $d_{\text{Pd atom}} = 0.4142·d_{\text{Pd atom}}$, at these locations (octahedral sites) and = 1·$d_{\text{Pd atom}}$, at the maximum opening (at Vac sites on corners of unit cells). The spread between opposed tetrahedral sites at $\frac{3}{4}$ $\frac{3}{4}$ $\frac{3}{4}$, and $\frac{3}{4}$ – $\frac{1}{4}$ – $\frac{1}{4}$, is the same as at the corner site (tube diameter = $d_{\text{Pd atom}}$, neglecting the size of the deuteron). This undulating diameter tube is a long mean free path for electron transport. In a regular FCC lattice there are no such straight line directions with uninterrupted openings for distances of more than 2$d_{\text{Pd atom}}$. They are long, yet intersecting channels of vacancies, as shown in Fig. 8.

The tube lattice (Fig. 8) has Pd atoms nested between the volumes defined by tube intersections: either Pd with D (H) or only Pd, depending on whether the phase is δ′ or δ. If it is δ, with D′ inside the tubes as ions (octahedral sites), then it is a variant of Storms’ model [44]: an electron
e in between each D+ ion (Fig. 9). The tube would keep the shielding aligned and set up the tube of D-e-D-e-D-e-D... for a resonance condition of linear one dimensional vibrating deuterons along the tube. This resonance condition was calculated [45] for a string of spring-connected masses (deuterons separated by negative charge as in δ phase). Resonance would allow the compressive forces on the deuterons to increase and inter-deuteron displacements to decrease without limit, yielding a NAE.

It has been understood that δ phase, with interstitial occupancy at octahedral sites, is more probable than δ′ phase with interstitial occupancy at tetrahedral sites near room temperature. This is possibly true for the lower D/Pd ratios (r<sub>x</sub>). However at high r<sub>x</sub>, this research, along with other research [5,6,19,22,24,37,46], suggests the reverse (tetrahedral more likely) since the volume fraction of δ′ (5%) is much higher than the volume fraction of δ (0.03%). Isaeva et al. [19] has indicated the phase change to tetrahedral site occupancy is a change with more order than that of octahedral site occupancy: tetrahedral site is favored as having more order.

Resistivity is larger in a disordered state than in an ordered state [47]. Neutron diffraction data of Ferguson et al. [6] and Pitt and Gray [5] show H (D) in both octahedral and tetrahedral sites, and groups of each phase, since the neutron beam would encounter groups of both phases. High D/Pd ratios have been harder to achieve historically, so SAV by room temperature electrolysis has not been produced (or at least recognized). If, in addition to merely having δ phase (necessary and sufficient), a requirement such as resonance is an additional

Fig. 6. Resistivity versus Temperature for Pd-H samples from low temperature to room temperature and extrapolated to temperatures above room temperature with a positive coefficient of resistivity. from Schindler et al. [41] and Tripodi et al. [42].

Fig. 7. The ordered unit cells of the delta (δ), Pd<sub>3</sub>VacD<sub>4</sub> and delta prime (δ′), Pd<sub>3</sub>VacD<sub>4</sub> phases. The main difference is that D occupies octahedral sites (x) in δ and tetrahedral sites (o) in δ′. Edges of the unit cell in δ′ are straight paths of open tunnels (or tubes) because of vacant Pd atoms. In δ, the only atoms in these tubes are D+ ions, but in δ′, the tubes are completely empty of all atoms.

Fig. 8. Tubes for each unit cells of either δ or δ′ phases. These phases form a 3-D vacancy tube lattice or network of intersecting tunnels. The tube lattice (green) has Pd and isotopic hydrogen in the space between tubes in δ′ (left image = Pd<sub>3</sub>VacD<sub>4</sub> – T), or has only Pd atoms and one central D atom (right image = Pd<sub>3</sub>VacD<sub>4</sub> – O) in the space with D+ inside the tubes in δ. Tube diameter varies from 0.4142 to 1 of Pd atom with wavelength (period) matching the unit cell. Only 1 of the 12 unit cell edges is shown with the undulating diameter tubes, but all 12 have them (2 wavelengths shown in each case). Unit cell images (blue and red) after Isaeva et al. [19].

Fig. 9. Storms [44] has modeled electron shielding in a two-dimensional crack shown on left and available online: https://www.youtube.com/watch?v=SNodilc6su0. The center shows that a string of alternating electrons and deuterons (protons) will buckle when left in a two-dimension crack with a third dimension of width of 1 atom. The present view of SAV in Figs. 7 to 9 corrects the buckling problem since the lattice tube is ≤ 1 atom in diameter and maintains alignment when compressed axially (see Staker [45]).
necessary condition to produce nuclear energy, then $f_v(\delta)$ could be larger than 0.03%. A nuclear reaction of lower energy (e.g., production of tritium and protium; but it cannot be the dominant reaction) would also make it larger, but only by a factor of 5.9 ($= 23.8 \text{ MeV}/4.04 \text{ MeV}$, making $f_v(\delta) = 0.18\%$). It must be emphasized that $\delta$ phase as a NAE is a very small volume fraction and could easily be absent or missed, explaining why evidence for LENR is often not found in the early replication attempts. Also since $\delta'$ phase is of such low volume fraction (total resistance of the bulk does not drop to zero), therefore $\delta'$ can be overlooked too. Light on these issues, should come from recent insight into the processing required to produce SAV [1,26] near room temperature in Pd and Ni, along with additional future research on the topic, especially DFT calculations of electron density inside the open undulating diameter Vac tubes.

5. Conclusions

(1) The volume fraction ($f_v$) of $\delta$ phase was estimated from the amount of nuclear energy measured. The volume fraction was $f_v(\delta) \approx 0.03\%$. Experimental measurements suggest that $\delta$ is the nuclear active environment (NAE) for low energy nuclear reactions (LENR).

(2) The volume fraction ($f_v$) of $\delta'$ phase was estimated from the measurement of the change in resistivity of the overall multiphase Pd-D alloy using the rule of mixtures. The volume fraction of $\delta'$ phase was $f_v(\delta') \approx 5\%$.

(3) The ordered structure of the unit cell of these SAV is simple cubic. There are very long strings of Pd vacancies, without even deuterons present in these tubes or channels. These are part of the $\delta'$ phase, and since calculations show the resistivity to be near zero, these long strings of Pd vacancies offer an environment that could support a high conducting state (phase).

(4) Which interstitial site (octahedral or tetrahedral) is occupied by isotopic hydrogen determines whether the SAV phase is potentially nuclear active or potentially highly electrically conductive. These two phases are distinct and can coexist as minor volumetric components (phases) because they share the same composition (same D/Pd ratio) and atomic arrangements of Pd atoms and lattice vacancy sites, and result from hydrogen-induced vacancy formation. Thus, portions of the specimen can potentially be producing nuclear energy (excess heat) while other portions are potentially highly electrically conductive.

Appendix A

Electrolysis current: voltage drop, and electromigration contribution

Consider a long cathode undergoing electrolysis while also undergoing an electromigration current $I$ along its length (Fig. A1). With the electrolysis current $i_T$ at zero, the voltage drop along the length, $\Delta V_{ei}$, is $IR$, where $R$ is total resistance of the rod and equal to $\rho L/A$, where $\rho$ is resistivity of the rod, $L$ its length, and $A$ its cross sectional area. Next consider the case where electromigration current is zero: $\Delta V_e$ is the integral of $dV$ from 0 to $L$, with $dV$ being the differential voltage drop across a differential element of the rod of length $dx$ located at a variable position $x$, so that $dV = R_i(dx) i$, where $R_i$ is the resistance per unit length of rod and $i$ is electrolysis current through the element at $x$. The current in the rod entering at the top of a differential element at $x$ is $i_T = i_T - i_T(x/L)$ where $i_T$ is the total electrolysis current impinging from the electrolyte onto the total surface area (full length) of the rod and $i_T(x/L)$ is that portion of electrolytic current below the differential element of length $dx$. This gives:

$$\Delta V_e = \int_0^L R_i i_T (1 - i_T(x/L)) dx = R_i i_T \int_0^L dx - R_i i_T \int_0^L x dx = R_i i_T L - \frac{R_i i_T}{2} L^2 - \frac{R_i i_T}{2} L^2 = \frac{1}{2} R_i i_T L$$

Fig. A1. A long thin cathode of cross section $A$ and length $L$ undergoing electrolysis current $i_T$ with an additional internal current $I$.  

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
This is as expected since the contribution of the voltage drop from the electrolyte current, as x changes from 0 to L, is linear with a minimum of 0, a maximum of R/L and an average value of R/L. Thus one half of the electrolysis current must be added to the electromigration current when determining the voltage drop for the specimen. But since (R/L) is R, the voltage drop with the combination of both electromigration current I and electrolysis current Iy, is AVvolt = R (I + Iy/2) = (pI/L) (I + Iy/2). This extra contribution to the voltage drop from electrolysis current also contributes to electromigration, making its largest contribution at the bottom of the specimen where it makes a contribution of twice the average value, and making basically zero contribution at the top. It is generally ignored in the table of concentration enhancement as a function of electromigration currents, but cannot be ignored when estimating voltage drop and resistivity.

References


