

# Insights into the relation between crystal structure and deuterium desorption characteristics of Pd–Au–D alloys

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## Abstract

Neutron diffraction and thermal desorption spectroscopy are used to determine the details in the crystallographic structure and the deuterium desorption characteristics of deuterated Pd–Au alloys. Compositions under investigation include alloys corresponding to both subcritical and supercritical conditions with respect to the  $\alpha$ – $\beta$  phase transitions. The effect of the Au-content on deuterium desorption properties is discussed in relation to the degree of deuterium loading and the phase diagram. Furthermore, the distribution of deuterium over the octahedral and tetrahedral interstitial sites is determined. The tetrahedral site occupancy increases with increasing Au content and is significant for both supercritical and subcritical phases.

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## 1. Introduction

One of the main technical challenges associated with the production of high-purity hydrogen at reduced costs is the development of highly selective hydrogen membranes. These membranes should withstand the demanding industrial conditions of high temperatures and pressures in multicomponent gaseous environments. Supported dense Pd-based membranes with a thickness of several micrometres are the most suitable options for this purpose [1]. However, the lifetime of pure Pd membranes in thermal cycles from operational conditions to room temperature is limited. Failure often occurs owing to deformation and fracture caused by the large specific volume change during

the hydride formation and decomposition processes. Several experimental and theoretical studies suggest that a longer operation lifetime can be achieved through the addition of specific alloying elements [1,2]. A lifetime in the order of years is essential for an economically viable process. Beneficial effects of alloying consist of: a reduction of the critical temperature for the transition from the  $\alpha$ -metal solid solution to the  $\beta$ -hydride phase, a smaller unit cell volume difference between the two phases, improved mechanical properties, and an enhanced resistance to surface poisoning, e.g., by sulfur compounds [1,2]. Furthermore, higher hydrogen solubility and diffusivity for many Pd alloys (e.g., alloys with Ag, Au or Cu) result in higher hydrogen permeability than in Pd itself [2]. The hydrogen solubility and the diffusion mechanism of hydrogen through these membranes are determined by the nature of the specific alloying elements, their concentration and distribution in the metal lattice, as well as by the (local)

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interaction of the hydrogen atoms with the alloying elements. Structural information of the phases formed during hydrogen absorption/desorption in Pd alloys is therefore crucial for understanding the effect of alloying on macroscopic hydrogen permeation behaviour. This formed the main motivation for investigating the effect of the crystal structure of hydrogenated (deuterated) Pd alloys and its relation with the desorption characteristics. Pd–Au alloys were chosen as a model system for this work, because they fulfil the requirements for promising membrane materials, and they are expected to show characteristic phenomena such as hydrogen-induced (short- and long-range) ordering transformations [3], interesting also from a fundamental point of view.

Pd and many of its alloys (with small content of alloying elements) crystallize in the face centred cubic (fcc) structure [4]. Two distinct types of interstitial sites available to hydrogen atom occupancy can be distinguished, namely the octahedral (O) and tetrahedral (T) positions. For the palladium–hydrogen system, studied for more than a century, it is commonly accepted that hydrogen atoms occupy exclusively the octahedral interstitial sites. This has been confirmed by early neutron diffraction (ND) studies on palladium–deuterium samples [5] and accepted by extension for the case of hydrogen atoms. A number of publications reporting ND studies on Pd–H(D) powders [5–8] or single crystals [9,10], and quasielastic neutron scattering studies of the hydrogen dynamics in palladium [11,12] support this conclusion. However, most of these structural studies have considered in their data analysis only the occupation of either the octahedral or the tetrahedral sites solely, and have shown that, within the limits of these two options, the O-site-only occupancy is most consistent with the experimental data. This clearly leaves open the occurrence of simultaneous occupation of O and T sites, which could possibly provide a better description of the ND data, especially at higher H(D) contents. Nevertheless, the hypothesis of octahedral site occupancy was further generalized for hydrogen in fcc Pd alloys. To the best of the authors' knowledge, however, there is no experimental evidence confirming this hypothesis for all relevant cases. In particular, for Pd–Au alloys, the limited amount of available ND data are from room temperature experiments and were interpreted in terms of O-site-only occupation in the  $\alpha$  phase [13]. To what extent this is valid for Pd–Au alloys with different Au contents and higher H(D) concentrations is therefore still unknown.

Theoretical studies on hydrogen in Pd and Pd alloys, in contrast, suggest that, depending on the alloying element and its concentration, the occupation of tetrahedral sites may occur. Moreover, it has also been suggested that T sites could act as transition states in the process of hydrogen diffusion. For hydrogen in pure Pd, first principles calculations have shown that, while occupation of T sites by hydrogen atoms is less favourable than occupation of O sites, because the potential energy of hydrogen at the T site is slightly higher than at the O site, hydrogen diffusion

between O sites necessarily occurs via passage of T sites. Furthermore, significant self-trapping of hydrogen at the T-site position can be induced, depending on the magnitude of both the local relaxation of Pd atoms around the T site and the vibrational energy of the interstitial species (H, D, T) [14–16]. Similar conclusions were drawn for H in Pd alloys. First principle calculations show that, in these cases, the local atomic arrangement of metal atoms in the nearest neighbourhood of the interstitial site is the dominant factor for the site occupancy and stability [17–20].

Experimental evidence supporting the simultaneous occupation of O and T sites is scarce and mostly controversial. Quasielastic neutron scattering measurements on  $\beta$ -Pd hydrides could be best described with a mixed occupation of O and T sites [21]. The proposed mechanism for hydrogen diffusion through palladium by hopping of H from O site to O site via intermediate T sites [21], rather than by direct O–O or T–T jumps as previously considered [11,12], sparked an extensive scientific discussion. An important step forward was made in recent in situ ND investigations on the Pd–D system in the supercritical region [22], presenting evidence that part of the deuterium atoms indeed occupy tetrahedral positions. In analysing their data, these authors considered a mixed octahedral and tetrahedral occupation, confirming conclusions of diffusion experiments [21] and first principles studies [14–16]. An important question is whether and to what extent T-site occupancy occurs in fcc Pd-based alloys, and whether it is limited to the supercritical region only, as inferred in Ref. [22] for the case of Pd.

The present study is designed to provide an answer to these questions. ND experiments were performed to investigate the crystal structure of deuterated Pd–Au alloys. The samples contained up to 25 at.% Au and were loaded with different amounts of deuterium at room temperature. Sample compositions in both subcritical and supercritical regions were selected on the basis of the room temperature ternary phase diagram (Fig. 1). Deuterium was used instead of hydrogen to avoid a high background due to the incoherent scattering of hydrogen. The Pd–Au–D system is very well suited for ND studies, as the constituent elements have sufficiently different cross sections for coherent neutron scattering (i.e.,  $b_{\text{Pd}} = 0.591$  barn,  $b_{\text{Au}} = 0.763$  barn,  $b_{\text{D}} = 0.6674$  barn).

The crystallographic properties determined by ND experiments are complemented by the hydrogen desorption characteristics obtained by thermal desorption spectroscopy (TDS) on the same materials. The combined information obtained from TDS and ND provides a clear insight into the relation between the effect of alloying on macroscopic properties and on the microscopic atomic structure, as discussed in this paper.

## 2. Experimental

Pd foils (99.95%, Goodfellow Metals) and foils of Pd–Au alloys containing 10, 20 and 25 at.% Au (Philips

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