Crystal structure of gold hydride

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ABSTRACT

A number of transition metal hydrides with close-packed metal sublattices of *fcc* or *hcp* structures with hydrogen in octahedral interstitial positions were obtained by the high-pressure-hydrogen technique described by Ponyatovskii et al. (1982). In this paper we consider volume increase of metals by hydrogenation and possible crystal structure of gold hydride in relation with the structure of mercury, the nearest neighbor of Au in the Periodic table. Suggested structure of AuH has a basic tetragonal body-centered cell that is very similar to the mercury structure Hg-*t I* 2. The reasons of stability for this structure are discussed within the model of Fermi sphere–Brillouin zone interactions.

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1. Introduction

Transition metals usually form hydrides with close-packed atomic arrangements (face centered cubic, *fcc*, or close-packed hexagonal, *hcp*) of metal atoms and interstitial arrangements (tetrahedral and/or octahedral) of hydrogen in the metallic host lattice. The experimental method of high-pressure high-temperature synthesis of metal hydrides is described in [1,2]. With this method, several hydrides MeH (Me – transition metals and transition metal alloys) have been synthesized in a gaseous hydrogen atmosphere at high pressure and temperature. Structural investigations of MeH revealed an increase of volume related to a metallic atom.

An interesting observation is that this volume increase is approximately the same for different metals ranging from $\sim$2 to $\sim$3 Å^3 per metal atom for the composition MeH. The volume expansion in metal hydrides was a subject of many discussions [2–6]. At first glance one could expect that the hydrogen-induced expansion of the metal lattice should be related to the ratio of the metal and hydrogen radii, the latter being assumed equal to $\sim$0.6 Å. However, experiment shows that the volume expansion is independent of the radii ratio and is larger than expected from the simple model of hard sphere packing assuming the occupation by small spheres (H) of the interstitial positions formed by large spheres (Me). Experimentally observed ΔV (Å^3) in transition metal hydrides [2] are listed in Table 1, where ΔV refers to one atom H. Note that the structures of all hydrides are *hcp* or *fcc*, except FeH with a double hexagonal close-packed structure (*dhcp*) [7]. In this paper, the volume increase due to hydrogenation is discussed in connection with the changes in the number of valence electrons accompanying the formation of hydrides.

An attempt to synthesize gold hydride was reported in [8] by annealing of pure gold in a hydrogen atmosphere at $\sim$50 kbar and $\sim$400 °C. The composition of synthesized material was estimated as AuH and an orthorhombic lattice was suggested. In this paper, we consider possible crystal structure of AuH in relation with the structure of mercury, the nearest neighbor of Au in the Periodic table. This suggestion is supposed assuming the atomic volume increase due to hydrogenation that is nearly equal to the volume increase by moving elements along the row in the Periodic table. The reasons of stability for this kind of structure are discussed with consideration of the Fermi sphere–Brillouin zone interactions within the nearly-free electron model.

2. Results and discussion

2.1. Correlations between the volume and hydrogen content of metal hydrides

The observed volume increase ΔV in metal hydrides can be understood by considering how the electron of hydrogen is involved in the valence band of the host metal consisting of *d* and *s* parts. Magnetic measurements on hydrides of transition metals have shown an increase of *d*-band filling by $\sim$0.5 electron per H atom [1–3]. The *s*-band filling is also expected to increase. The increase in the number of *s* valence electrons is responsible for the increase in the atomic volume of metal hydrides. Atomic volumes of transition metals are nearly insensitive to the filling of the *d*-band and the volume increase correspond to addition of $\sim$0.5 *s*-electron per H atom.

The value of volume expansion per one *s* valence electron can be estimated from the volume relations in the post-transition (or *sp*) elements shown in Fig. 1 [9]. These elements have filled *d*-shells, which form ionic cores with the nearly equal size for the elements

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Table 1
Volume increase accompanying the formation of monohydrides of metals of the 3d and 4d rows (results from Ref. [2]).

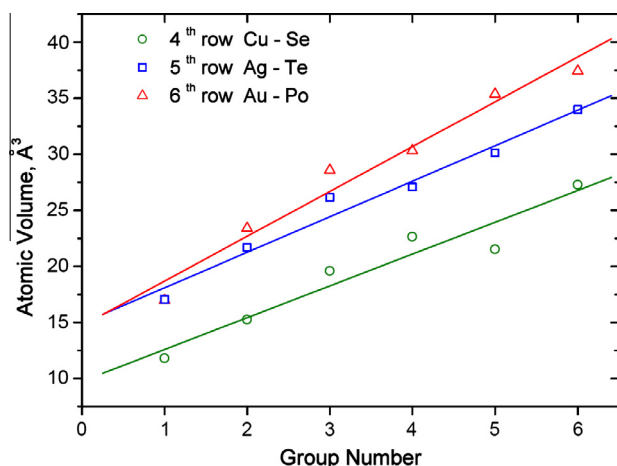| MeH	Cell	ΔV (Å³)	MeH	Cell	ΔV (Å³)
CrH	hcp	2.2	MoH	hcp	2.2
MnH	hcp	1.8	TcH	hcp	2.0
FeH	dhcp	1.9	–	–	–
CoH	fcc	1.8	RhH	fcc	2.4
NiH	fcc	2.2	PdH	fcc	2.4

Fig. 1. Atomic volumes of the *sp* elements of 4-th, 5-th and 6-th rows of the Periodic table; structural data are taken from [9]. Nearly linear increase of the atomic volume along one row demonstrates the nearly constant "valence electron volume" (the volume per one valence electron).

from one row of the Periodic table. For the elements in one row, the atomic volumes increase nearly linearly with increasing group numbers equal to the numbers of valence *sp* electrons. The change in the atomic volume is associated with the number of *sp* outer electrons, as was considered by Schubert and called the "valence electron volume" [10] (see Fig. 2).

Estimations from plots in Fig. 1 give the volume per one *s* electron ∼4–∼5 Å³. Thus, the volume increase $\Delta V \sim 2$ Å³ in transition metal hydrides corresponds to ∼0.5 electron increase in the *s*-band as expected from experimental studies [1–3].

It is interesting to compare volumes of PdH and the neighboring to Pd element Ag. Both volumes are equal to ∼17.1 Å³ that points

to the nearly equal number of valence *s* electrons in PdH and Ag. Recently, a platinum hydride has been synthesized under high hydrogen pressure. The hydride had a close-packed hexagonal structure [11,12] and lattice parameters $a = 2.779$ Å and $c = 4.731$ Å at $P = 30.5$ GPa. The volume difference between the platinum hydride and Pt metal was $\Delta V = 2.09$ Å³ and therefore corresponded to the PtH composition [12]. It should be noted that PtH is structurally similar to the neighboring to Pt element–gold, which accepted the *hcp* structure at pressures above 250 GPa [13].

A special case is the AuH hydride reported to be synthesized by Antonov et al. [8]. Elements Cu, Ag and Au continue transition metal rows and have their *d*-band already filled. Therefore the additional electron from hydrogen dissolved in these metals should go to the *s*-band. One could expect that the addition of one valence electron to Au will make the atomic volume and crystal structure of AuH similar to those of Hg, the neighboring element of Au in the Periodic table.

2.2. Suggested structure for gold hydride

The position of gold in the Periodic table is in the group I B right after the transition metals. The electron energy levels of gold correspond to the completely filled $5d^{10}$ band and one electron is on the 6s level. The crystal structure of gold is face-centered cubic, the same as that of the neighboring transition metals (Ir, Pt) and group I B metals (Cu, Ag). The elements of the II B group have considerably different structures. Particularly, Hg has a rhombohedrally distorted *fcc* structure at normal pressure and a tetragonally distorted *bcc* structure at pressure above 3.4 GPa. The latter structure of Hg (space group $I4/mmm$, two atoms in the unit cell, Pearson symbol $t I 2$) can be retained at atmospheric pressure and at 77 K and has $a = 3.995$ Å; $c = 2.825$ Å; $c/a = 0.707$; atomic volume 22.54 Å³ [9].

An analysis of the diffraction pattern for AuH (Fig. 3) revealed the possibility of indexing the group of strong diffraction peaks on the base of a tetragonal body-centered cell with lattice parameters $a = 3.933$ Å and $c = 2.782$ Å, $c/a = 0.707$, atomic volume 21.5 Å³ assuming two atoms in the unit cell. This structure is very similar to the mercury structure Hg-$t I 2$ as compared in Table 2. The pure gold has the atomic volume 17.0 Å³, so the volume increase due to the formation of hydride is 4.5 Å³, which is approximately twice that for the transition metal hydrides. This agrees with the assumption discussed above that the electrons supplied by the hydrogen atoms all go to the *s*-band of the metals like Au with the already filled *d*-band, but are shared in approximately equal quantities of ∼0.5 el. per H atom between the *d*- and *s*-bands in the transition metals, in which the *d*-band is partly empty.
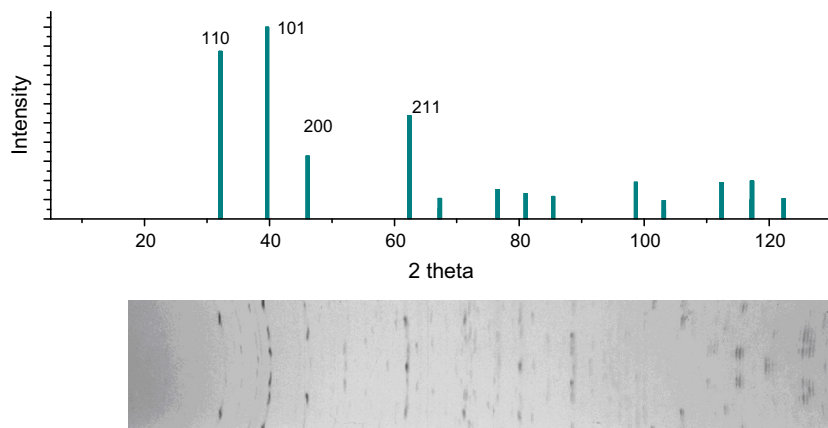

Fig. 2. Experimental diffraction pattern of one of the Au sample hydrogenated under high pressure (bottom of the figure) and a calculated pattern for the tetragonal structure $t I 2$ similar to that of β-Hg with the lattice parameters given in Table 2. Cu Kα radiation, room temperature.