High-pressure synthesis of tantalum dihydride

Mikhail A. Kuzovnikov,[1,2,*] Marek Tkacz,[1] Haijing Meng,[1] Dmitry I. Kapustin,[2,3] and Valery I. Kulakov[2]
[1]*Institute of Physical Chemistry PAS, 44/52 Kasprzaka, 01-224 Warsaw, Poland*
[2]*Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow District, Russia*
[3]*Moscow State University, Leninskie gory, 119992 Moscow, Russia*
(Received 19 July 2017; revised manuscript received 26 September 2017; published 26 October 2017)

The reaction of tantalum with molecular hydrogen was studied by x-ray diffraction in a diamond-anvil cell at room temperature and pressures from 1 to 41 GPa. At pressures up to 5.5 GPa, a substoichiometric tantalum monohydride with a distorted bcc structure was shown to be stable. Its hydrogen content gradually increased with the pressure increase, reaching H/Ta = 0.92(5) at 5 GPa. At higher pressures, a new dihydride phase of tantalum was formed. This phase had an hcp metal lattice, and its hydrogen content was virtually independent of pressure. When the pressure was decreased, the tantalum dihydride thus obtained transformed back to the monohydride at $P = 2.2$ GPa. Single-phase samples of tantalum dihydride also were synthesized at a hydrogen pressure of 9 GPa in a toroid-type high-pressure apparatus, quenched to the liquid-N_2 temperature, and studied at ambient pressure. X-ray diffraction showed them to have an hcp metal lattice with $a = 3.224(3)$ and $c = 5.140(5)$ Å at $T = 85$ K. The hydrogen content determined by thermal desorption was H/Ta = 2.2(1).

DOI: 10.1103/PhysRevB.96.134120

I. INTRODUCTION

Most hydrides of *d* metals are formed in wide concentration ranges and can be considered as solid solutions of hydrogen-occupying interstitial positions in the metal lattice [1]. Until recently, hydrides with the maximal H-to-metal atomic ratio of $x \approx 2$ (dihydrides) were known for five transition metals from groups IV and V (Ti, Zr, Hf, V, and Nb, respectively [1]), and all these dihydrides could be formed at room temperature and hydrogen pressures lower than 10 bars (10^{-3} GPa). At the same time, the maximal hydrogen solubility ever observed in the group-V element tantalum only reached $x = 0.86$ at 1.6 GPa and 400 K [2]. Thanks to the development of the methods of compressing molecular hydrogen in diamond-anvil cells (DACs) to pressures of tens of gigapascals, a number of new hydrides of *d* metals have been synthesized in the past few years, including unexpected dihydrides (RhH_2 [3] and FeH_2 [4]), trihydrides (FeH_3 [4], IrH_3 [5], $NbH_{2.5}$, and NbH_3 [6]), and even higher FeH_5 hydride [7].

Recent *ab initio* calculations predicted that a TaH_2 dihydride with an hcp metal lattice and $P6_3mc$ symmetry of the full crystal structure should be thermodynamically stable in the hydrogen pressure range of 0–50 GPa and further transform to TaH_4 at higher pressures [8].

The present paper reports on the synthesis of tantalum dihydride achieved at a hydrogen pressure of 5.5 GPa and room temperature in a diamond-anvil cell and examined by *in situ* x-ray diffraction. Additionally, much larger samples of the dihydride weighing 50–100 mg each were synthesized at a hydrogen pressure of 9 GPa using a toroid-type high-pressure apparatus. The samples were quenched to the liquid-N_2 temperature and recovered to ambient pressure that allowed a direct measurement of their hydrogen content by thermal desorption.

II. EXPERIMENTAL DETAILS

Samples for the DAC and toroid experiments were cut from 99.9% tantalum foils with thicknesses of 10 and 160 μm, respectively. Before the high-pressure experiment, the sample was scratched with a sharp scalpel to remove the oxidized surface layer. Removing this layer dramatically improved the kinetics of hydrogenation.

The DAC experiments were carried out at pressures up to 41 GPa and room temperature. The DAC cell, the gas loading system, and the *in situ* energy-dispersive x-ray diffraction (EDXRD) setup were the same as in our previous experiments [9]. Hydrogen was always in excess, serving both as a reagent and as the pressure-transmitting medium. The pressure was determined with an accuracy of ± 0.3 GPa from a ruby-R1 fluorescence line using the quasihydrostatic pressure scale by Mao *et al.* [10]. X-ray powder diffraction was measured using polychromatic radiation from a conventional tungsten target tube [11] collimated down to about 100 μm. Using an intensity monitor of unscattered radiation, the x-ray beam was positioned at the center of the gasket hole with an accuracy of 10 μm before each EDXRD measurement. With the hole size being no less than 120 μm at the highest pressure of 41 GPa, this procedure therefore ensured that the gasket was not illuminated by the beam at any measured pressure. The x-ray scattering angle 2θ was set at about 18° and calibrated at the beginning of each experiment using a diffraction pattern of the hydrogen-free initial bcc Ta foil at ambient pressure. The resolution of the setup was $\Delta d/d \approx 5\%$. Accumulating a diffraction pattern at any given pressure required about 1 day. The lattice parameters of the synthesized Ta-H phases were obtained by the Le Bail refinement of experimental energy-dispersive XRD patterns normalized to a constant background level. At pressures above 10 GPa, the XRD measurements typically were accompanied by a pressure drift of about 1 GPa. These were the final pressure values that will further be indicated in the paper as the measuring pressures of the DAC experiments.

A few samples of tantalum dihydride assigned for *ex situ* measurements and weighing 50–100 mg each were

*kuz@issp.ac.ru

synthesized at 9 GPa and 100 or 150 °C in a toroid-type high-pressure chamber [12] using NH_3BH_3 as an internal hydrogen source; the method of hydrogenation is described elsewhere [13]. The temperature was measured with a chromel-alumel thermocouple to an accuracy of ±10 °C; the pressure was determined accurate to ±0.5 GPa using a preliminary calibration of the high-pressure apparatus against the ram load. After the hydrogenation was finished, the sample was cooled together with the chamber to the liquid-N_2 temperature; the pressure was released; the chamber was disassembled under liquid nitrogen; the sample was recovered from the chamber and further stored in liquid nitrogen in order to prevent hydrogen losses.

The hydrogenated samples thus prepared were examined by XRD at 85 K with a powder Siemens D500 diffractometer using Cu $K\alpha$ radiation selected by a diffracted beam monochromator. The diffractometer was equipped with a home-designed nitrogen cryostat that permitted loading the samples from the liquid-N_2 bath without intermediate warming. The obtained diffraction patterns were analyzed by the Rietveld profile refinements method using the POWDERCELL2.4 software.

The thermal stability and the total hydrogen content of the samples were determined by hot extraction of the hydrogen into a preevacuated calibrated volume in the regime of heating the sample from −186 to 650 °C at a rate of 10 °C min^{-1} [14]. The mass of the analyzed probe was a few milligrams; the accuracy in determining the atomic ratio $x = \mathrm{H/Ta}$ was $\delta x/x = 5\%$.

III. RESULTS AND DISCUSSION

A. DAC experiments

Figures 1 and 2 show some energy-dispersive x-ray diffraction patterns of tantalum in a hydrogen atmosphere measured in the course of a stepwise increase and decrease in pressure, respectively. After changing the pressure, the sample was equilibrated for about 1 h, and the diffraction pattern then was accumulated during approximately 1 day. The maximal pressure attained in this series of measurements was 41.1 GPa.

The experiment started with loading the DAC by hydrogen at $P = 1.4$ GPa, resulting in a considerable shift of the broad diffraction peaks of bcc tantalum to higher d values (compare the patterns labeled 0 and 1.4 GPa in Fig. 1). The face-centered orthorhombic (space-group $Fmmm$, $a = 4.83$, $b = 4.79$ Å $\approx a$, and $c = 3.46$ Å $\approx a/\sqrt{2}$ [2]) crystal structure of a metal lattice of the nonstoichiometric monohydride TaH_{1-x}, which is known to form at this pressure, can be considered as a distorted bcc lattice. Because of the low resolution of our energy-dispersive XRD measurements, we did not observe the splitting of individual peaks resulting from the lattice distortions. The atomic volumes of the orthorhombic monohydride presented in Fig. 3 as a function of pressure were estimated from the mean lattice parameter of its pseudo-bcc unit cell.

As one can further see from Fig. 1, the XRD pattern of the Ta-H sample changed qualitatively at $P = 5.5$ GPa due to the formation of a new phase with an hcp metal lattice. This new phase was likely to be a tantalum dihydride because its formation from tantalum monohydride was accompanied by approximately the same volume expansion as the formation of monohydride from pure tantalum [compare the steps at 5.5 and 1.4 GPa in the $V(P)$ dependence composed by the solid symbols in Fig. 3]. At $P > 5.5$ GPa, the atomic volume $V(P)$ of the dihydride monotonically decreased with increasing pressure, whereas the axial ratio of its hcp unit cell remained virtually unchanged and equal to $c/a = 1.59(1)$, which is somewhat less than the ideal value of $c/a = \sqrt{8/3} \approx 1.633$.

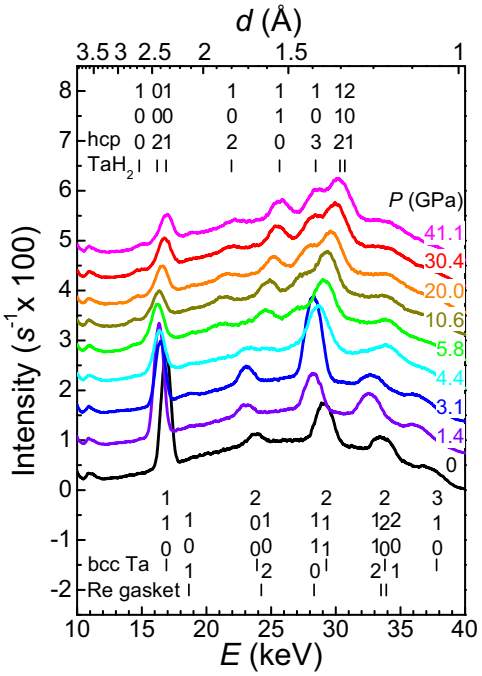

FIG. 1. Energy-dispersive x-ray diffraction patterns of tantalum (shifted vertically for clarity) in a hydrogen atmosphere measured in the course of a stepwise pressure increase in a DAC. The peaks at $E < 12$ keV are the L fluorescence emission lines from tantalum; the other peaks are of a diffraction origin. The ticks at the bottom of the figure indicate calculated peak positions for Ta at ambient pressure (bcc lattice with $a = 3.30$ Å) and positions of the strongest diffraction peaks from the hydrogen solution in rhenium at $P = 5$ GPa (hcp metal lattice with $a = 2.79$ and $c = 4.41$ Å [15]). The ticks at the top show the positions of the strongest peaks from the hcp tantalum dihydride at $P = 41.1$ GPa ($a = 3.08$ and $c = 4.88$ Å).

The $V(P)$ values of the tantalum dihydride measured at decreasing pressure (open symbols in Fig. 3) well agree with the $V(P)$ dependence constructed at increasing pressure. The dihydride could not however be recovered to ambient pressure at room temperature and decomposed back into the tantalum monohydride (compare the patterns labeled 2.6 and 2.2 GPa in Fig. 2). The decomposition pressure $P = 2.2(4)$ GPa was determined more accurately in the second series of measurements within a smaller pressure range up to 9 GPa (blue triangles in Fig. 3). Determining the decomposition pressure is significant for the thermodynamics of the Ta-H system because the equilibrium pressure for the ternary "hydrogen gas" + "lower hydride" + "higher hydride" equilibria is likely to be much closer to the decomposition pressure of the higher hydride than to the midpoint between the pressures of its formation and decomposition [17].

The pressure-volume data for the hcp tantalum dihydride were fitted to the Murnaghan equation of state $V(P) = V_0(1 + PB_0'/B_0)^{-1/B_0'}$ [18] and to the third-order Birch-

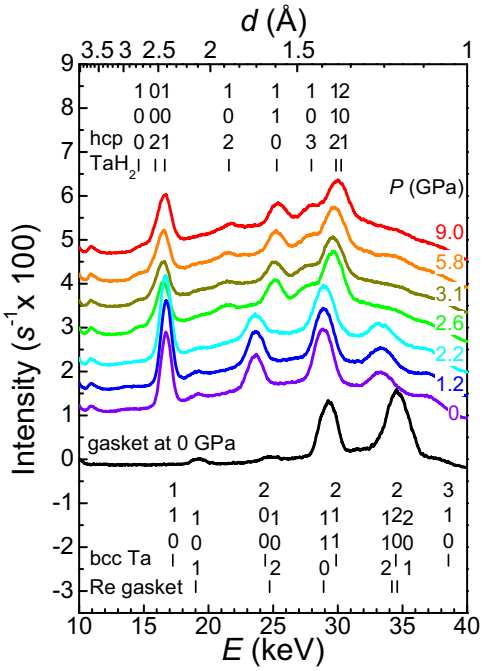

FIG. 2. Energy-dispersive x-ray diffraction patterns of tantalum (shifted vertically for clarity) in a hydrogen atmosphere collected in the course of a stepwise pressure decrease in the second series of measurements with the maximal pressure of 9 GPa. The top ticks show the positions of the strongest peaks for the hcp tantalum dihydride at $P = 9$ GPa ($a = 3.19$ and $c = 5.07$ Å). The black curve labeled "gasket at 0 GPa" shows a diffraction pattern from the strongly textured rhenium gasket measured after decompressing the cell to ambient pressure. Other commentaries are the same as in the caption for Fig. 1.

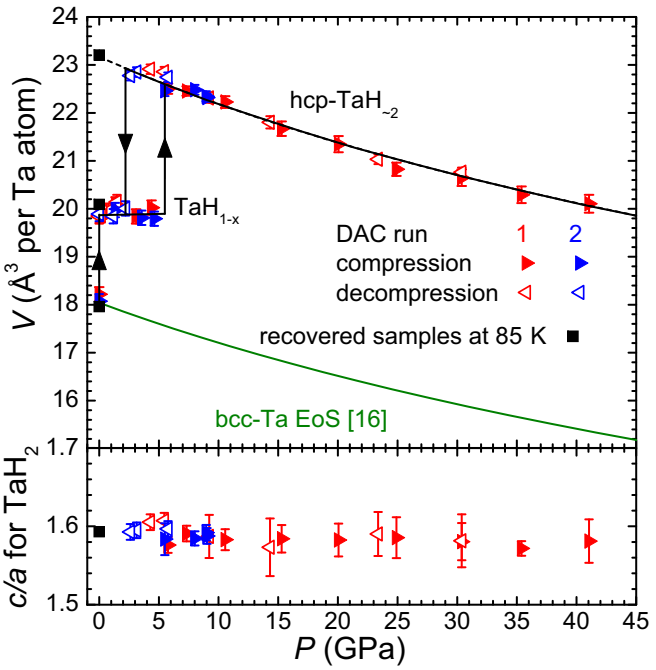

FIG. 3. The top panel: The pressure-volume dependencies for Ta under high hydrogen pressure. The vertical black lines with arrows indicate the pressures of phase transitions. The solid black curve and its dashed prolongation to ambient pressure show the equation of state (EoS) fit for $TaH_{\sim 2}$ with the fitting parameters listed in Table I. The solid olive line at the bottom of the panel shows the EoS for Ta in an argon medium [16]. The bottom panel: The c/a ratios for the hcp $TaH_{\sim 2}$. The black squares show V_0 and c/a for the recovered $TaH_{\sim 2}$ and TaH_{1-x} samples and initial Ta measured at 85 K and ambient pressure, see Sec. III B.

Murnaghan equation $P(V) = \frac{3B_0}{2}[(\frac{V}{V_0})^{-7/3} - (\frac{V}{V_0})^{-5/3}]\{1 + \frac{3}{4}(B_0' - 4)[(\frac{V}{V_0})^{-3/2} - 1]\}$ [19] using the value of $B_0' = 4$ of the bulk modulus pressure derivative typical of many metals and alloys. Using these equations gave virtually the same values of the fitting parameters V_0 and B_0, which are indicated in Table I. The EoS of $TaH_{\sim 2}$ thus obtained is shown by the solid black curve in Fig. 3.

As seen from Fig. 3 and Table I, the value of $V_0 = 23.2(2)$ Å^3 per Ta atom resulted from fitting the $V(P)$ high-pressure data well agrees with the atomic volume of 23.14(4) Å^3 per Ta atom of tantalum dihydride synthesized in a toroid-type high-pressure chamber and examined by x-ray diffraction at ambient pressure and $T = 85$ K (this *ex situ* experiment is described in the next section of the paper). The obedience of the experimental $V(P)$ dependence to the Murnaghan equation suggests that the hydrogen content of the tantalum dihydride should be nearly independent of pressure in the studied pressure range up to 41 GPa because varying the hydrogen content would lead to strong deviations from that equation (see, e.g., results for the hcp hydrides with varying compositions in the Mo-H [9] and W-H [20] systems).

B. *Ex situ* studies of recovered Ta-H samples

In order to directly determine the hydrogen content of the hcp tantalum dihydride, a few samples made of a much thicker Ta foil than in the DAC experiments (160 vs 10 μm^2) were loaded with hydrogen in a toroid-type apparatus at a pressure of 9 GPa and recovered to ambient pressure after cooling to the liquid-N_2 temperature. The phase composition of the samples was examined by x-ray diffraction at 85 K, and their mean H-to-metal atomic ratio was measured with a relative accuracy of 5% by thermodesorption of hydrogen into a preevacuated measuring system.

A 1-day exposure of the Ta sample to a hydrogen pressure of 9 GPa at room temperature only gave us the usual orthorhombic tantalum monohydride, presumably, due to the low kinetics of the formation of the dihydride from the thick foil. A 1-day exposure to the same pressure and 250 °C also produced the monohydride, presumably, due to the increase in the formation pressure of the dihydride with increasing temperature. Samples composed mostly of the dihydride and containing not more than a few percent of the monohydride were obtained by exposing the Ta foil for 1 day to 150 °C. Single-phase samples of the hcp tantalum dihydride were synthesized steadily at a hydrogen pressure of 9 GPa by holding the sample for 1 day at 150 °C and for another day at 100 °C.

An XRD pattern of one of the single-phase samples of tantalum dihydride is shown at the bottom of Fig. 4. For comparison, Fig. 4 also presents diffraction patterns of pure Ta (upper panel) and tantalum monohydride prepared at 5 GPa and 150 °C (middle panel). The samples of the

TABLE I. Atomic volume V_0, bulk modulus B_0, and its pressure derivative B_0' at ambient pressure obtained for $TaH_{\sim 2}$ and Ta as fitting parameters of the equation of state and by the *ex situ* measurements.

	Equation of state fits at 300 K			Recovered samples at 85 K
Substance	V_0 Å^3 per Ta atom	B_0 GPa	B_0'	V_0 Å^3 per Ta atom
bcc Ta in Ar	18.04 [16]	195(5) [16]	3.4(1) [16]	17.96(3)
hcp $TaH_{\sim 2}$ in H_2	23.2(2)	210(20)	4 (fixed)	23.14(4)

mono- and dihydride were very brittle, and we powdered them under liquid N_2 before the x-ray examination in order to diminish the texture effects. For the same purpose, the x-rayed sample of pure Ta was prepared from the powder of monohydride degassed by annealing in vacuum at 650 °C.

Figure 5 shows thermodesorption curves for the recovered single-phase samples of tantalum mono- and dihydride. The hydrogen content of the new hcp tantalum dihydride was found to be H/Ta = 2.2(1) and therefore noticeably exceeded the stoichiometric ratio H/Ta = 2. As one can see from Fig. 5, the decomposition of $TaH_{2.2}$ is a two-stage process. First, the sample abruptly released more than half of its hydrogen Δ(H/Ta) ≈ 1.3 in a narrow temperature interval near $T = -75$ °C and transformed to monohydride with H/Ta ≈ 0.9. The formation of the monohydride was confirmed by the x-ray diffraction study of a probe heated to −60 °C and quenched to the liquid-N_2 temperature. Intensive desorption of hydrogen from the monohydride thus produced began at about 100 °C and continued up to about 400 °C (open circles in Fig. 5). The sample of the monohydride prepared at 5 GPa demonstrated a somewhat higher thermal stability and fully decomposed after heating to about 550 °C (open squares in Fig. 5). The decreased thermal stability of the monohydride formed from the decomposed dihydride is typical of metal hydrides subjected to hydrogenation/dehydrogenation cycling [21,22]. The effect usually is attributed to the disruption of the surface oxide layer limiting the rate of dehydrogenation and to the formation of fresh noncontaminated surfaces due to cracking of the sample caused by its large expansion and contraction during the hydrogenation/dehydrogenation cycle.

The formation of the orthorhombic solid solutions of hydrogen in tantalum was shown earlier to be accompanied by a linear volume increase with a slope of about 2.4 Å^3 per H atom at H/Ta ⩽ 0.86 [2,23–27]. As one can see from Fig. 6, the hydrogen-induced volume expansion of the orthorhombic monohydride $TaH_{0.92}$ and hcp dihydride $TaH_{2.2}$ synthesized and studied in the present paper well agree with such a linear dependence. The Vegard law is therefore applicable to the Ta-H system in the whole studied composition range of 0 ⩽ H/Ta ⩽ 2.2.

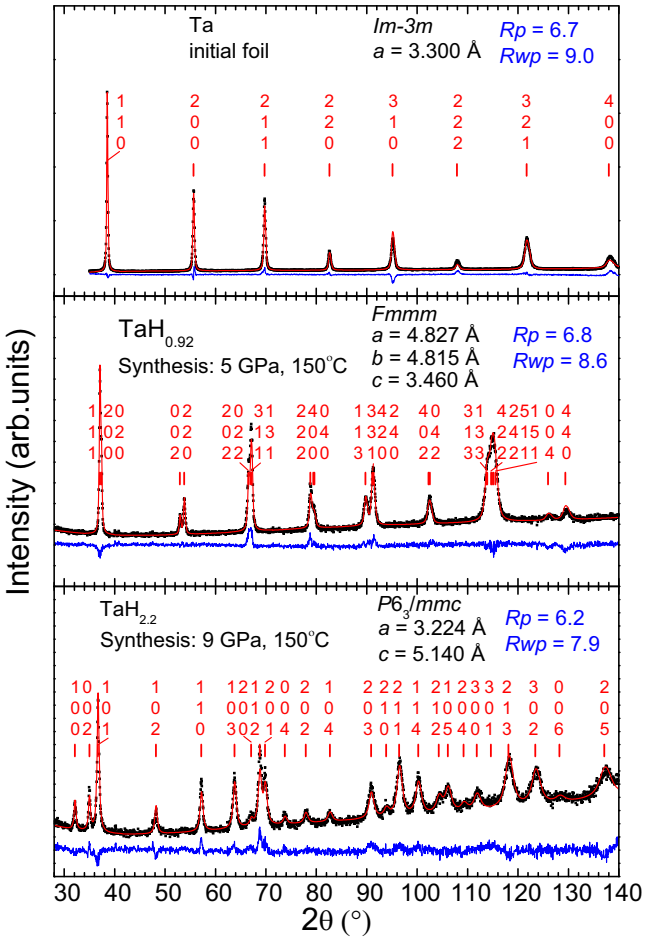

FIG. 4. XRD patterns of the initial Ta foil (top) and Ta samples hydrogenated at 5 GPa (middle) and 9 GPa (bottom) at 150 °C. Ambient pressure $T = 85$ K, Cu $K\alpha$ radiation. The black points stand for the experimental data, the red curves show the Rietveld fits, and the blue curves are the fit residuals. The rather large residual R factors are mostly due to the large grain size and strong texture of the samples.

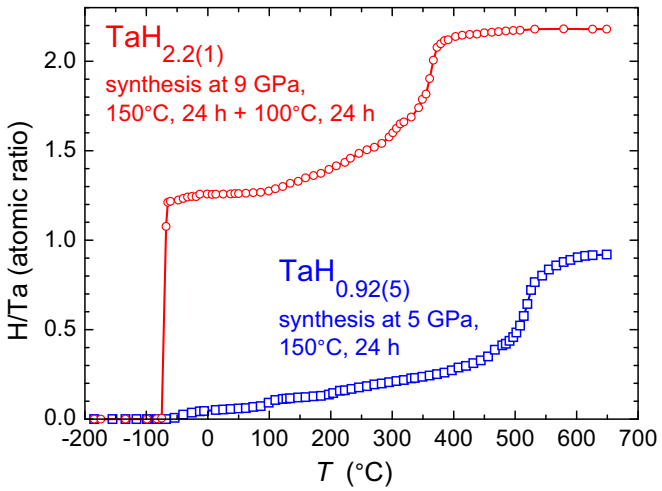

FIG. 5. Hydrogen release from the recovered $TaH_{2.2}$ and $TaH_{0.92}$ samples heated in vacuum at a rate of 10 °C/min.

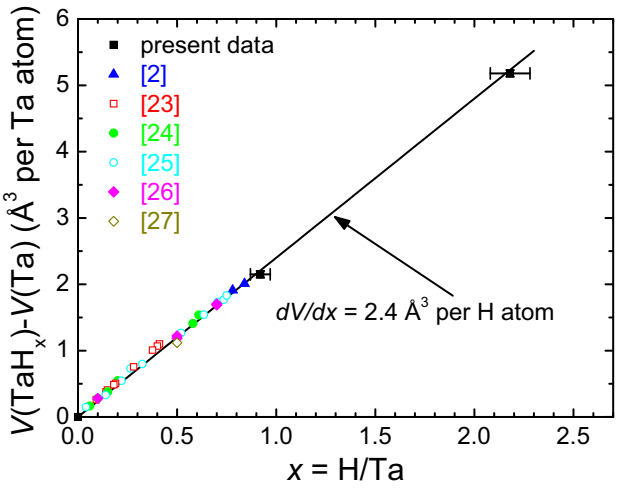

FIG. 6. Lattice expansion of Ta upon hydrogenation. The black symbols stand for the present data; the other colors are for the literature data [2,23–27]. The uncertainty in V is smaller than the symbol size.

The hcp crystal structure is typical of alkaline-earth-metal dihydrides under sufficiently high pressures. For the rare-earth and transition-metal dihydrides, the fcc crystal structure is more common. In fact, the hcp structure was found only in two rare-earth-metal dihydrides EuH_2 [28] and YbH_2 [29]. Among the transition-metal dihydrides, the hcp crystal structure was observed only in NbH_2 at pressures above 40 GPa [6]. The NbH_2 and VH_2 dihydrides are predicted to form hcp phases at a similar pressure [30].

Ab initio calculations also predicted that molybdenum [31] and tungsten [20] should form hcp dihydrides at 9 and 60 GPa, respectively. Experiments however showed that the hcp hydrides of these metals were essentially nonstoichiometric and their maximal hydrogen content did not exceed H/Me = 3/2 [9,20].

Recently, a few new nonstoichiometric and overstoichiometric hydrides were synthesized in the Nb-H system under high pressure: fcc $NbH_{2.5-3}$, hcp $NbH_{2.5}$, double hcp (dhcp) $NbH_{2.5}$, and distorted bcc NbH_3 [6]. At present, it is not clear which of these phases are stable because none of them was observed in a single-phase state. The analysis is complicated further because different experimental runs gave different sequences of phase transformations.

In the present paper, we did not observe phases with $x \geqslant 2.5$ in the Ta-H system. Presumably, they could be formed at higher pressures. *Ab initio* calculations by Zhuang *et al.* [8] underestimated the equilibrium formation pressure of TaH_2 (0 GPa instead of our experimental estimate of 2.2 GPa). One, therefore, can expect that the formation pressure of higher hydrides also considerably will exceed 50 GPa proposed for TaH_4 [8].

In the hcp lattice of tantalum dihydride with the a and c parameters listed at the bottom of Fig. 4, the shortest intersite separation distance of $c/4 = 1.28$ Å is that between the tetrahedral sites, which form short-spaced pairs. According to the well-established Switendick rule, the minimal distance between hydrogen atoms should not be much less than 2 Å in any transition metal [32]. Consequently, no more than half of the tetrasites in the hcp $TaH_{\sim 2}$ could be occupied by hydrogen atoms due to the mutual blocking. Since there are two tetrasites per each metal atom in the hcp lattice, the maximal number of H atoms accommodated at the tetrasites is equal to the number of metal atoms. The same number of H atoms can be accommodated at the octasites, therefore, the total hydrogen content of the hcp tantalum dihydride should not exceed H/Ta = 2 if the Switendick rule is valid. The arrangement of $\delta x \sim 0.2$ of the extra H atoms in the crystal structure of our samples of $TaH_{2.2}$ remains an open problem. We believe that further neutron-diffraction investigations could suggest an answer. For example, the formation of a large number of stacking faults in the hcp metal lattice of $TaH_{2.2}$ could be a possible solution. Note in this connection that in the double hcp lattice formed by alternating hcp and fcc layers of metal atoms, the shortest H-H distance is realized between the tetrasites and the octasites that allows the hydride to have H-to-metal atomic ratios of up to $x = 2.5$ (a structure of this type has recently been proposed for the dhcp $NbH_{2.5}$ [6]).

Tantalum is a superconductor with the critical temperature of $T_c = 4.46$ K [33], and its hydrogenation up to H/Ta ≈ 0.5 was shown earlier to monotonically decrease T_c [34]. Recent *ab initio* calculations predicted [8] that TaH_4 with T_c values of 23.9-31 K should be stable at hydrogen pressures of 50-250 GPa and further transforms to TaH_6 with $T_c =$ 124.2–135.8 K. It also was predicted that, at pressures 0–50 GPa, the most stable hydride should be a $P6_3mc$ TaH_2 phase with the hcp metal lattice similar to that of the hcp $TaH_{2.2}$ phase synthesized in the present paper. Regretfully, the superconducting properties of $P6_3mc$ TaH_2 were not analyzed.

To examine if the unusual hcp structure of tantalum dihydride gives rise to superconductivity, we performed magnetic ac susceptibility measurements at ambient pressure on the virgin Ta foil and quenched $TaH_{0.92}$ and $TaH_{2.2}$ samples using the technique described elsewhere [35]. Within the measured temperature range of 4.4–300 K, we observed the onset of superconductivity in the Ta foil at $T_c = 4.44$ K in fair agreement with the data in literature [33] and no superconducting transition both in $TaH_{0.92}$ and in $TaH_{2.2}$. The absence of superconductivity in the orthorhombic monohydride $TaH_{0.92}$ is consistent with earlier experimental results [34].

IV. CONCLUSIONS

Compared to other d metals of the IV group (vanadium and niobium), tantalum forms dihydride at a much higher hydrogen pressure, and this dihydride has an hcp metal lattice instead of the fcc one.

The new tantalum dihydride has an overstoichiometric composition of H/Ta = 2.2(1) as measured by thermodesorption. In contrast to the Nb-H phases [6], the atomic volumes of both the orthorhombic monohydrides and the hcp dihydride of tantalum well obey the Vegard law.

Luckily, single-phase samples of tantalum dihydride can be recovered to ambient pressure if cooled to the liquid-N_2 temperature. This allows an accurate investigation of many properties of the dihydride by conventional techniques including the determination of its full crystal structure by neutron diffraction. The work is in progress.

ACKNOWLEDGMENTS

This work partly was supported by the Russian Foundation for Basic Research under Grant No. 17-02-01142. The authors thank A. V. Palnichenko (ISSP RAS) for the superconductivity measurements.

[1] Y. Fukai, *The Metal-Hydrogen System*, 2nd ed. (Springer-Verlag, Berlin/Heidelberg, 2005).
[2] A. W. Szafrański, M. Tkacz, S. Majchrzak, and H. Züchner, J. Less-Common Met. **101**, 523 (1984).
[3] B. Li, Y. Ding, D. Y. Kim, R. Ahuja, G. Zou, and H.-K. Mao, Proc. Natl. Acad. Sci. USA **108**, 18618 (2011).
[4] C. M. Pépin, A. Dewaele, G. Geneste, P. Loubeyre, and M. Mezouar, Phys. Rev. Lett. **113**, 265504 (2014).
[5] T. Scheler, M. Marqués, Z. Konôpková, C. L. Guillaume, R. T. Howie, and E. Gregoryanz, Phys. Rev. Lett. **111**, 215503 (2013).
[6] G. Liu, S. Besedin, A. Irodova, H. Liu, G. Gao, M. Eremets, X. Wang, and Y. Ma, Phys. Rev. B **95**, 104110 (2017).
[7] C. M. Pépin, G. Geneste, A. Dewaele, M. Mezouar, and P. Loubeyre, Science **357**, 382 (2017).
[8] Q. Zhuang, X. Jin, T. Cui, Y. Ma, Q. Lv, Y. Li, H. Zhang, X. Meng, and K. Bao, Inorg. Chem. **56**, 3901 (2017).
[9] M. A. Kuzovnikov, H. Meng, and M. Tkacz, J. Alloys Compd. **694**, 51 (2017).
[10] H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res.: Solid Earth **91**, 4673 (1986).
[11] M. Tkacz, S. Majchrzak, and B. Baranowski, High Pressure Res. **6**, 85 (1990).
[12] L. G. Khvostantsev, V. N. Slesarev, and V. V. Brazhkin, High Pressure Res. **24**, 371 (2004).
[13] V. E. Antonov, B. M. Bulychev, V. K. Fedotov, D. I. Kapustin, V. I. Kulakov, and I. A. Sholin, Int. J. Hydrogen Energy **42**, 22454 (2017).
[14] I. O. Bashkin *et al.*, JETP Lett. **79**, 226 (2004).
[15] T. Atou and J. V. Badding, J. Solid State Chem. **118**, 299 (1995).
[16] H. Cynn and C.-S. Yoo, Phys. Rev. B **59**, 8526 (1999).
[17] V. E. Antonov, A. I. Latynin, and M. Tkacz, J. Phys.: Condens. Matter **16**, 8387 (2004).
[18] F. D. Murnaghan, Proc. Nat. Acad. Sci. USA **30**, 244 (1944).
[19] F. Birch, Phys. Rev. **71**, 809 (1947).
[20] T. Scheler, F. Peng, C. L. Guillaume, R. T. Howie, Y. Ma, and E. Gregoryanz, Phys. Rev. B **87**, 184117 (2013).
[21] R. Wiswall, in *Hydrogen in Metals II*, edited by G. Alefeld and J. Völkl (Springer, Berlin, 1978), pp. 212–215.
[22] A. Andreasen, T. Vegge, and A. S. Pedersen, J. Phys. Chem. B **109**, 3340 (2005).
[23] H. Peisl, in *Hydrogen in Metals I*, edited by G. Alefeld and J. Völkl (Springer, Berlin, 1978), pp. 53–74.
[24] F. Ducastelle, R. Caudron, and P. Costa, J. Phys. Chem. Solids **31**, 1247 (1970).
[25] B. Stalinski, Bull. Acad. Pol. Sci. Cl. III **2**, 245 (1954).
[26] R. Yamada, N. Watanabe, K. Sato, H. Asano, and M. Hirabayashi, J. Phys. Soc. Jpn. **41**, 85 (1976).
[27] H. Asano, Y. Ishikawa, and M. Hirabayashi, J. Appl. Crystallogr. **11**, 681 (1978).
[28] T. Matsuoka, H. Fujihisa, N. Hirao, Y. Ohishi, T. Mitsui, R. Masuda, M. Seto, Y. Yoda, K. Shimizu, A. Machida, and K. Aoki, Phys. Rev. Lett. **107**, 025501 (2011).
[29] J. S. Olsen, B. Buras, L. Gerward, B. Johansson, B. Lebech, H. L. Skriver, and S. Steenstrup, Phys. Scr. **29**, 503 (1984).
[30] C. Chen, F. Tian, D. Duan, K. Bao, X. Jin, B. Liu, and T. Cui, J. Chem. Phys. **140**, 114703 (2014).
[31] X. Feng, J. Zhang, H. Liu, T. Iitaka, K. Yin, and H. Wang, Solid State Commun. **239**, 14 (2016).
[32] A. C. Switendick, in *Transition Metal Hydrides*, edited by R. Bau, Advances in Chemistry Vol. 167 (ACS, Washington, DC, 1978), pp. 264–282.
[33] J. G. C. Milne, Phys. Rev. **122**, 387 (1961).
[34] F. H. Horn and W. T. Ziegler, J. Am. Chem. Soc. **69**, 2762 (1947)
[35] N. S. Sidorov, A. V. Palnichenko, D. V. Shakhrai, V. V. Avdonin, O. M. Vyaselev, and S. S. Khasanov, Physica C **488**, 18 (2013).