

High-Pressure Synthesis and Characterization of Iridium Trihydride

Thomas Scheler,¹ Miriam Marqués,² Zuzana Konôpková,³ Christophe L. Guillaume,¹
Ross T. Howie,¹ and Eugene Gregoryanz^{1,*}

¹Centre for Science at Extreme Conditions, School of Physics and Astronomy, The University of Edinburgh,
Edinburgh EH9 3JZ, United Kingdom

²MALTA Team and Departamento de Química Física y Analítica, Universidad de Oviedo, E-33006 Oviedo, Spain

³DESY Photon Science, Notkestrasse 85, 22 607 Hamburg, Germany

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We have performed *in situ* synchrotron x-ray diffraction studies of the iridium-hydrogen system up to 125 GPa. At 55 GPa, a phase transition in the metal lattice from the fcc to a distorted simple cubic phase is observed. The new phase is characterized by a drastically increased volume per metal atom, indicating the formation of a metal hydride, and substantially decreased bulk modulus of 190 GPa (383 GPa for pure Ir). *Ab initio* calculations show that the hydrogen atoms occupy the face-centered positions in the metal matrix, making this the first known noninterstitial noble metal hydride and, with a stoichiometry of IrH₃, the one with the highest volumetric hydrogen content. Computations also reveal that several energetically competing phases exist, which can all be seen as having distorted simple cubic lattices. Slow kinetics during decomposition at pressures as low as 6 GPa suggest that this material is metastable at ambient pressure and low temperatures.

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High pressure as a general route to material synthesis [1–3] has been used in the past to obtain hydride phases of most transition metals under thermodynamic equilibrium conditions [4,5]. However, in particular for the noble metals, the required pressures can be substantial (with the sole exception of palladium [6]). So far, the highest reported pressures for hydride synthesis are 25 GPa for tungsten [7,8] and 27 GPa for platinum hydride [9]. Most known *d*-metal hydrides exhibit a closed-packed metal host lattice with hydrogen atoms occupying the octahedral or tetrahedral interstitial sites, the former being by far the most common modification [5]. Thus, these hydrides usually exhibit a hydrogen:metal (H:*M*) ratio close to 1, with few exceptions where higher ratios are achieved (e.g., rhodium dihydride [10]). No hydride phases are known for the noble metals silver, gold [11], osmium, and iridium. Interstitial hydrogen alloys are interesting due to their potentially important physical properties, such as modified crystalline structures and mechanical properties [12], altered microstructure [8] (nanocrystallinity), hydrogen mediated superconductivity [13,14], or potential hydrogen storage capabilities [10,15,16]. Furthermore, according to theoretical predictions, hydrogen confined in a host matrix might undergo the elusive transition to a metallic ground state at considerably lower pressures than pure hydrogen [17], which is expected to metallize above 375 GPa [18]—pressures still out of reach of current static compression techniques.

The formation of a hydride phase is readily observed in x-ray diffraction (XRD) measurements as an expansion of the unit cell (see, e.g., in rhenium [12]), or a structural phase transition with increased volume per metal atom

compared to the parent metal (e.g., bcc to hcp in tungsten [7,8,19] or fcc to hcp in platinum [9]). It has been found that, due to contributing its electron to the valence band of the surrounding metal, the presence of one hydrogen atom expands the host lattice by 2–3 Å³ (depending on the material, see Refs. [4,5]). From the formation of the nitrides of iridium and osmium [20] at conditions identical to those at which platinum nitride forms [21], it could be argued that an equivalent behavior might be observed for hydrogen. However, although platinum hydride readily forms at 27 GPa, no hydride phases of iridium or osmium are known.

We have performed XRD studies on iridium in a hydrogen medium at pressures up to 125 GPa in the diamond anvil cell (see the Supplemental Material [22] for details). At 55 GPa an additional phase appears in XRD patterns of iridium. The new phase can easily be indexed in the *Pm* $\bar{3}$ *m* space group (simple cubic, see Fig. 1) and exhibits a significantly larger volume per atom than pure iridium at the same pressure. This indicates the formation of a compound material, i.e., a metal hydride (as opposed to a phase transition in pure iridium). At 65 GPa, the volume difference amounts to ~ 6.6 Å³ per metal atom, substantially more than usually observed for interstitial metal hydrides (e.g., 2.1 Å³ for platinum hydride [9]). Direct comparison with other metal hydrides suggests a H:*M* ratio of 3 (assuming full stoichiometry). However, such comparisons are not directly valid since estimating the hydrogen content by comparing unit-cell volumes is based on *empirical* findings in *interstitial* hydrides. The simple cubic lattice does not exhibit comparable interstitial sites. At room temperature, the formation of the new phase progresses

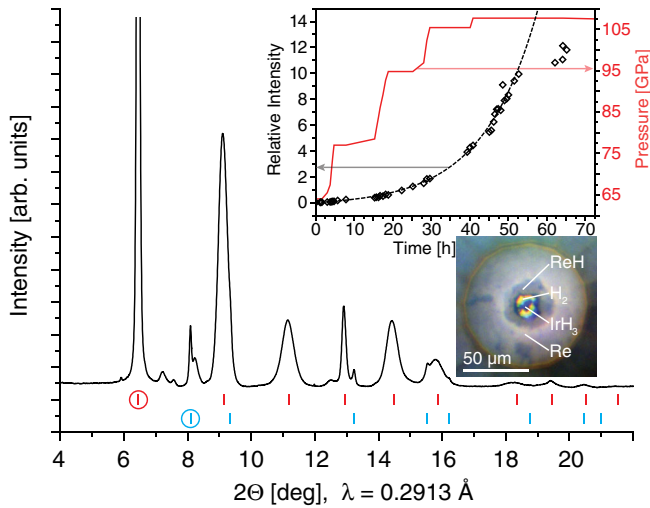


FIG. 1 (color online). Integrated x-ray diffraction pattern at 120 GPa, indexed with simple cubic iridium hydride ($a = 2.591 \text{ \AA}$, upper red tick marks) and fcc iridium ($a = 3.577 \text{ \AA}$, lower blue tick marks). Other visible reflections stem from rhenium hydride formed at the gasket rim. The inset shows the development over time of the relative scattering intensity (left-hand scale) of the IrH_3 (001) peak compared to the Ir (111) peak (circled reflections in the diffraction pattern). The dashed line indicates an exponential guide to the eye to the data up to $t = 50 \text{ h}$. The solid red line denotes the applied pressure (right-hand scale). The optical micrograph shows the gasket and sample at 100 GPa. The extension of the rhenium hydride zone in the gasket is clearly visible.

very slowly at first and accelerates exponentially over time during the first 50 h after crossing synthesis conditions (see inset of Fig. 1). The transition was measured through the relative scattering intensities between Bragg peaks belonging to the hydride phase and parent material measured in the same diffraction pattern. Interestingly, the progress is independent of pressure. During this period, pressure was increased to 110 GPa with no deviation from exponential growth detectable. However, after 50 h, the formation process slows down. Even after 2 weeks at 110 GPa, pure Ir is still present in the sample volume. We therefore employed low-power single-sided laser heating to accelerate the formation process. Indeed, within a few minutes, the parent material had completely vanished and only the hydride phase remained. Because of the low laser power applied ($< 6 \text{ W}$), temperature measurement was not possible but could only be estimated to be below 1000 K. In a subsequent experiment, we repeated the laser heating process at 55 GPa and achieved almost complete transformation of the sample within ca. 30 min. It should be noted here that, when pure Ir is compressed to similar pressures, it remains in the fcc configuration [23] and does not adopt any of the phases observed in this experiment and discussed in detail below.

On decompression we found the hydride phase of iridium to be visible to pressures as low as 6 GPa, with onset

of decomposition visible between 15 and 20 GPa (indicated by a decrease in scattering intensity). Thus, we were able to establish the equation of state of this phase in the pressure range between 6 and 125 GPa. The data were fitted to a Vinet-type equation of state yielding a zero-pressure volume $V_0 = 23.33 \text{ \AA}^3$ and a surprisingly low zero-pressure bulk modulus $B_0 = 190(3) \text{ GPa}$ [$B'_0 = 5.62(11)$] (see Fig. 2). This corresponds to a Ir-H distance of 2.021 \AA at zero pressure. A similar change in mechanical properties is only known for chemically produced hexagonal copper hydride where the bulk modulus drops from 142 to 70 GPa, a phenomenon attributed to the hydrogen-metal bond which is partly covalent and ionic [24,25]. However, copper hydride still exhibits a closed-packed structure. No other hydride is known to exhibit a simple cubic host lattice which makes it difficult to establish the correct crystal structure by comparison, i.e., determine the position of the hydrogen atoms which are almost invisible to x rays. We therefore employed *ab initio* computational methods to address crystal structure, thermodynamic properties, and stability of this material. Assuming the $Pm\bar{3}m$ space group (Ir atoms located on the $1a$ sites), there are three potential stoichiometries IrH_n , $n = 1-3$. Taking the experimentally observed volume at 81 GPa ($V = 18.59 \text{ \AA}^3$), placing a single hydrogen atom on the

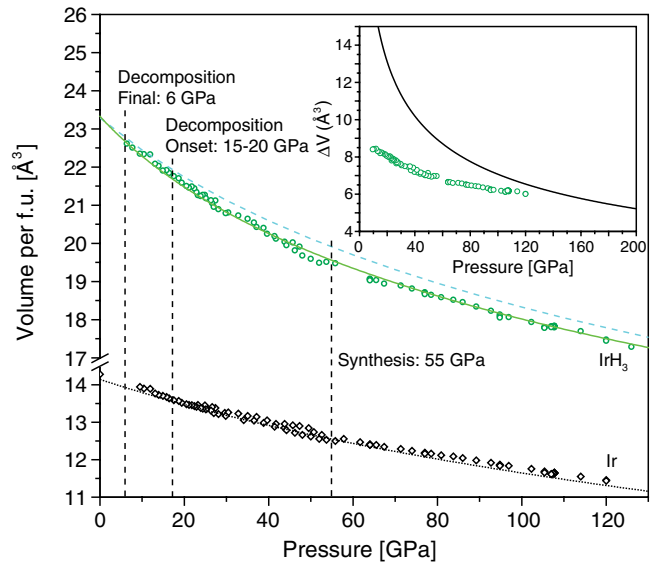


FIG. 2 (color online). Measured pressure-volume data of iridium (black diamonds) and iridium hydride (green circles). The dotted black line is a literature equation of state of iridium ($V_0 = 14.145 \text{ \AA}^3$, $B_0 = 383 \text{ GPa}$, $B'_0 = 3.1$, see Refs. [20,23]). The solid green line is a Vinet fit to our data [$V_0 = 23.33 \text{ \AA}^3$, $B_0 = 190(3) \text{ GPa}$, $B'_0 = 5.62(11)$], the dashed blue line the calculated equation of state of IrH_3 using the revised Tao-Perdew-Staroverov-Scuseria (rev-TPSS) approach for the $Pm\bar{3}m$ structure ($V_0 = 23.291 \text{ \AA}^3$, $B_0 = 249.9 \text{ GPa}$, $B'_0 = 4.32$). Inset shows the volume difference between IrH_3 and Ir in comparison to the equation of state for free hydrogen (solid line, showing volume for three hydrogen atoms, adapted from Ref. [31]).

1*b* site yielded a calculated pressure of -0.5 GPa while three hydrogen atoms on the 3*d* sites lead to a pressure of 324.6 GPa. Therefore, these two configurations can be ruled out as possible candidates. A derived layered structure with only two of the three available 3*c* sites occupied [IrH₂, *P4/mmm*, Ir(1*a*), H(2*e*)] would correspond to a somewhat plausible pressure of 49.8 GPa. However, it is well known that calculations employing the Perdew-Burke-Ernzerhof (PBE) functional slightly overestimate the pressure and better agreement (98.5 GPa) is found for the IrH₃ structure with hydrogens occupying the 3*c* sites (for more details, see the Supplemental Material [22]).

It can therefore be concluded that the hydrogen atoms most probably occupy the center of the faces [3*c* sites at coordinates $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$, and $(\frac{1}{2}, \frac{1}{2}, 0)$] in the simple cubic metal lattice [iridium atoms occupy the 1*a* sites at coordinates (0,0,0)], making this phase iridium trihydride. The calculated parameters for the equation of state are $V_0 = 23.739 \text{ \AA}^3$, $B_0 = 238.3$ GPa, $B'_0 = 4.36$. The difference to the calculated volume of pure iridium at 65 GPa is 7 \AA^3 , in good agreement with experimental data. The calculated volume is 1.75% larger than the experimental value, which is typical for density-functional theory (DFT) generalized-gradient calculations. However, the bulk modulus is unexpectedly larger than the one found in fitting an equation of state to our experimental data. When constraining $B' = 4$ in fitting the equation of state to our experimental data, a bulk modulus of $B_0 = 231$ GPa is found. However, the quality of fit deteriorates drastically, rendering this value significantly less plausible. Thus, to test if the lower experimental bulk modulus arises from a not-fully stoichiometric phase, we also calculated the equation of state of IrH_{2.875}, modeled by creating a single hydrogen vacancy on a $2 \times 2 \times 2$ supercell of the simple cubic phase. However, its compressibility turned out to be very close to that of the fully stoichiometric IrH₃ phase ($B_0 = 240$ GPa). Although we cannot exclude a deviation from ideal stoichiometry at higher pressures, it does not seem physically reasonable. Even if site vacancies exist in the synthesized material, taking into account the overestimation of the volume linked to the use of the PBE functional, the H:M ratio would still be very close to 3.

Interestingly, the *Pm* $\bar{3}$ *m* structure does not emerge as dynamically stable, with phonon softening in all the high-symmetry points at low pressures and in *M* and *X* at high pressures (see Figs. 1 and 2 in the Supplemental Material [22]). Freezing in the atomic distortions involved in these soft modes leads to several structures with lower enthalpies [see Fig. 3(a)]. For instance, the unstable M_3^- mode that consists of the closing and elongation of two of the *C*₂ axes of the Ir-Ir₆ octahedra yields to a *P4/nmm* structure involving a doubling of the simple cubic unit cell. It exhibits imaginary phonons at Γ (see Fig. 3 in [22]), related to a lowering of the symmetry to the *P4*₂*1**m* space group, where 2/3 of the hydrogen atoms deviate from the center

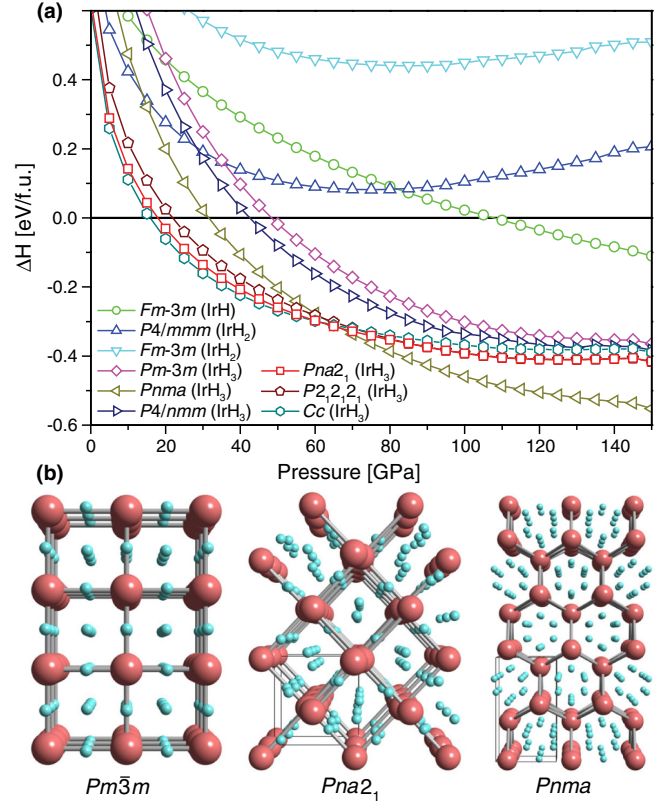


FIG. 3 (color online). (a) Calculated enthalpies of formation as a function of pressure for proposed iridium hydride structures. The enthalpy of the constituent elements at the corresponding pressure is taken as the reference enthalpy. $\Delta H = H(\text{IrH}_n) - H(\text{Ir}) - nH(0.5\text{H}_2)$. (b) Atomic framework in the *Pm* $\bar{3}$ *m* structure (left), *Pna*2₁ structure (middle), and *Pnma* structure (right). Details of the positioning for *Pna*2₁ and *Pnma* can be found in Table I in the Supplemental Material [22]. Larger red spheres denote iridium atoms, smaller blue spheres hydrogen atoms.

of the cube faces. It corresponds, in fact, to the condensation of the M_3^- and M_2^+ modes. Moreover, the simultaneous condensation of the M_3^- , M_2^+ , and X_5^- modes leads to a *P2*₁*2*₁*2*₁ structure without imaginary frequencies (see Fig. 4 in [22]). This soft-phonon-derived sequence involves a volume expansion of 0.65% at 125 GPa (increasing towards lower pressure, e.g., 4.64% at 40 GPa). Therefore, the lowering of enthalpy is energetically driven and related to stronger Ir-H interactions as the breaking of the degeneracy of the 12 nearest neighbor Ir-H distances and the shortening of some indicate (see Table I in [22]).

From structural searches (see the Supplemental Material [22] for details), two competitive structures (*Pna*2₁ and *C*_c) appear as thermodynamically stable below 68 GPa at 0 K. These dynamically stable structures (see Figs. 5 and 6 in [22]) are also distortions of the simple cubic lattice with decreased distortion amplitude when increasing pressure. It can be noted that the observed diffraction peaks exhibit varying degrees of broadening which is not explained by a strain or size effect. However, the broadening can be

explained by overlapping doublets or triplet peaks of these distorted simple cubic structures, in which the positions of the iridium atoms deviate slightly from their ideal positions in a simple cubic cell (see Table I in Ref. [22]). In fact, the $Pna2_1$ structure is dynamically stable at 125 GPa and a Le Bail fit yields good agreement with experimental data (see Figs. 7 and 8 in Ref. [22]). However, this structure can not be confirmed as a unique solution given the variety of structures energetically competitive and very similar to the simple cubic structure at that pressure. They are also associated with small hydrogen displacements in contrast to the proposed nearly isoenthalpic phases in heavy metal hydrides with mobile and structurally quite different layers of hydrogen molecules [26]. Moreover, in spite of the similar common metallic subarray, no reminiscent electrone behavior as reported in Ref. [27] is present in this case. Instead, all these structures ($P4/nmm$, Cc , $P2_12_12_1$, etc.) can be derived from the Cu_3Au -type structure typical of metallic alloys and are susceptible to be stabilized by local stress, thermal and anharmonic effects. Particularly, entropic and anharmonic contributions might help to reduce the distortion amplitudes and, ultimately, stabilize less distorted structures than those computationally predicted at 0 K. For instance, the symmetrization of the $P2_12_12_1$ structure towards the $Pnma(1)$ structure (see Table I in the Supplemental Material [22]) is confirmed when zero point energies (ZPEs) are considered. It can still be concluded that the present structure is most probably not perfectly simple cubic but rather slightly distorted.

At pressures above 68 GPa, a different phase with $Pnma$ space group emerges as energetically preferred at 0 K and dynamically stable (see Figs. 10 and 11 in the Supplemental Material [22]). When vibrational effects at 125 GPa are included, it becomes even more favorable, primarily due to a ZPE ≈ 50 meV/f.u. lower than that of the distorted simple cubic phases (note that the ZPEs of the slightly distorted simple cubic structures are within less than 1 meV/atom from each other, which is less than DFT accuracy). This structure, which still exhibits a H:M ratio of 3, is not a simple distortion of the simple cubic lattice (see Fig. 1 and Table I in Ref. [22]). Although the metallic atoms are hexaconnected as in the (distorted) simple cubic structures, the motif of iridium octahedra with hydrogens located close to the center of the edges transforms to one of triangular prisms with interstitial H_3 clusters with short distances in between (at 125 GPa, the shortest H-H distance is 1.46 Å, while it is 1.85 Å for the simple cubic structure). We do not see any experimental evidence for this phase in our data up to 125 GPa. It can be assumed that, similarly to other hydride phases, the formation is hindered by an energy barrier, which also accounts for the large hysteresis between synthesis and decomposition in the cubic phase. It has been suggested that a higher observed synthesis pressure compared to the calculated equilibrium pressure is due to the additional energy

required to dissociate the hydrogen molecule and macroscopically expand the metal sample (which requires energies comparable to the yield strength of the metal) [28]. Therefore, it could well be possible that the distorted cubic phase transforms into this phase at pressures above 125 GPa, while a high kinetic barrier could prevent the transformation in the observed pressure range. Taking into account that experiments are performed at room temperature, it is also plausible that the observable structure remains trapped in any of the local minima of the flat energy surface in the vicinity of the simple cubic structure. It should also be noted that, although the $Fm\bar{3}m$ IrH structure becomes stable against decomposition at 113 GPa in agreement with previous calculations [29], its enthalpy of formation is clearly less negative than those of the proposed IrH₃ structures. Therefore, the IrH₃ is the most stable stoichiometry throughout the studied pressure range.

It is interesting to compare the differences between iridium hydride and other transition metal hydrides: In most known d -metal hydrides, synthesized at high pressures, the hydrogen atoms occupy the octahedral or tetrahedral interstitial sites in the closed-packed metal host lattices. On these sites, hydrogen appears to be mostly incompressible and the mechanical behavior of the hydride is almost identical to that of the parent material. In iridium hydride, however, the presence of the hydrogen atoms has profound impact on the material's mechanical properties, decreasing the bulk modulus significantly. It is sometimes observed that the formation process in other hydrides is slow but can usually be accelerated by increasing pressure (e.g., in tungsten or rhenium), which is not observed here. Decomposition usually happens rapidly (instantaneously within the time scale of the experiment, i.e., usually <5 min) as soon as pressure falls below equilibrium conditions. Again, this is not observed in IrH₃ where decomposition happens slowly. Since formation is accelerated at higher temperatures, it can be assumed that the material might be “frozen” at lower temperatures and decomposition prevented, rendering it (meta)stable at ambient pressure (similar to copper hydride). The calculated elastic constants for the simple cubic structure ($Pm\bar{3}m$) at zero pressure ($C_{11} = 460.63$ GPa, $C_{12} = 127.54$ GPa, $C_{44} = 24.31$ GPa) of IrH₃ obey the Born stability criteria for the mechanical stability and inform on its metastability. It is also interesting to note the high Zener anisotropy [$2C_{44}/(C_{11} - C_{12}) = 0.15$] of this material and, especially, its low shear modulus (59.07 GPa, under the Voigt-Reuss-Hill approximation [30]), in contrast to the high value (210 GPa) for pure fcc iridium. Thus, one can conclude that the hydrogenation process turns a brittle material into a ductile material. The observation of the high hydrogen content in conjunction with a severely increased compressibility lends itself to the debate of whether the confined hydrogen might be compressed to

densities surpassing the proposed metallization density. However, a direct comparison between the equations of state for iridium and iridium hydride shows that the volume difference approaches a constant value in the high-pressure limit corresponding to pure hydrogen at ~ 250 GPa, well below predicted metallization pressures (see also the inset of Fig. 2).

In conclusion, we have synthesized a novel metal hydride from the elements with very high hydrogen content and unusual crystalline structure (distorted simple cubic metal host lattice) that is seen up to the highest pressures reached in this study (125 GPa). The formation of the lowest-enthalpy phase above 68 GPa (*Pnma* space group) is not observed and might be hindered by an energy barrier. The transition into the hydride phase as well as its decomposition are characterized by slow kinetics, which suggests that the material might be metastable at ambient pressure and low temperatures. The results presented in this work have important implications for the synthesis of new materials at high pressures and the study of metal hydrides in general, and we hope that our findings will encourage further experimental and theoretical work.

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*Corresponding author.

e.gregoryanz@ed.ac.uk

- [1] P.F. McMillan, *Nat. Mater.* **1**, 19 (2002).
- [2] V.L. Solozhenko and E. Gregoryanz, *Mater. Today* **8**, 44 (2005).
- [3] V.V. Brazhkin, *High Press. Res.* **27**, 333 (2007).
- [4] V.E. Antonov, *J. Alloys Compd.* **330**, 110 (2002).
- [5] Y. Fukai, *The Metal-Hydrogen System* (Springer-Verlag, Berlin, 2005).
- [6] B.B. Baranowski, *Platinum Met. Rev.* **16**, 10 (1972).
- [7] H. Kawamura, T. Moriwaki, Y. Akahama, and K. Takemura, in *Proceedings of the Joint 20th AIRAPT-43rd EHPRG International Conference on High Pressure Science and Technology, Karlsruhe, 2005* (E. Dinjus, Karlsruhe, Germany, 2005).
- [8] T. Scheler, F. Peng, C.L. Guillaume, R. T. Howie, Y. Ma, and E. Gregoryanz, *Phys. Rev. B* **87**, 184117 (2013).
- [9] T. Scheler, O. Degtyareva, M. Marqués, C.L. Guillaume, J.E. Proctor, S. Evans, and E. Gregoryanz, *Phys. Rev. B* **83**, 214106 (2011).
- [10] B. Li, Y. Ding, D. Y. Kim, R. Ahuja, G. Zou, and H.-K. Mao, *Proc. Natl. Acad. Sci. U.S.A.* **108**, 18 618 (2011).
- [11] The synthesis of gold hydride was reported in V.E. Antonov, *Dokl. Akad. Nauk SSSR* **266**, 376 (1982), but has not been confirmed since then [*Dokl. Phys. Chem.* **266**, 722 (1982)]; we studied gold under hydrogen atmosphere at pressures up to 120 GPa and did not observe any signs of hydride formation [C. Donnerer, T. Scheler, and E. Gregoryanz, *J. Chem. Phys.* **138**, 134507 (2013)].
- [12] T. Scheler, O. Degtyareva, and E. Gregoryanz, *J. Chem. Phys.* **135**, 214501 (2011).
- [13] H. Hemmes, A. Driessen, R. Griessen, and M. Gupta, *Phys. Rev. B* **39**, 4110 (1989).
- [14] I.O. Bashkin, V.E. Antonov, and E.G. Ponyatovsky, *Cuprates and Some Unconventional Systems*, Studies of High Temperature Superconductors Vol. 45 (Nova Science Publishers, New York, 2003), Vol. 1, pp. 171–241.
- [15] B. Sakintuna, F. Lamari-Darkrim, and M. Hirscher, *Int. J. Hydrogen Energy* **32**, 1121 (2007).
- [16] I. P. Jain, C. Lal, and A. Jain, *Int. J. Hydrogen Energy* **35**, 5133 (2010).
- [17] N. W. Ashcroft, *Phys. Rev. Lett.* **92**, 187002 (2004).
- [18] R. T. Howie, C.L. Guillaume, T. Scheler, A. F. Goncharov, and E. Gregoryanz, *Phys. Rev. Lett.* **108**, 125501 (2012); R.T. Howie, T. Scheler, C.L. Guillaume, and E. Gregoryanz, *Phys. Rev. B* **86**, 214104 (2012).
- [19] P. Zaleski-Ejgierd, V. Labet, T. A. Strobel, R. Hoffmann, and N. W. Ashcroft, *J. Phys. Condens. Matter* **24**, 155701 (2012).
- [20] A. F. Young, C. Sanloup, E. Gregoryanz, S. Scandolo, R.J. Hemley, and H.-K. Mao, *Phys. Rev. Lett.* **96**, 155501 (2006).
- [21] E. Gregoryanz, C. Sanloup, M. Somayazulu, J. Badro, G. Fiquet, H.-K. Mao, and R.J. Hemley, *Nat. Mater.* **3**, 294 (2004).
- [22] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.111.215503> for further details.
- [23] H. Cynn, J. E. Klepeis, C.-S. Yoo, and D. A. Young, *Phys. Rev. Lett.* **88**, 135701 (2002).
- [24] M. Tkacz and R. Burtovyy, *J. Alloys Compd.* **404**, 368 (2005).
- [25] J. Filipek, *Adv. Sci. Lett.* **19**, 1 (2007).
- [26] P. Zaleski-Ejgierd, R. Hoffmann, and N. W. Ashcroft, *Phys. Rev. Lett.* **107**, 037002 (2011).
- [27] A. Shamp, J. Hooper, and E. Zurek, *Inorg. Chem.* **51**, 9333 (2012).
- [28] V.E. Antonov, I. Latynin, and M. Tkacz, *J. Phys. Condens. Matter* **16**, 8387 (2004).
- [29] G. Gao, H. Wang, L. Zhu, and Y. Ma, *J. Phys. Chem. C* **116**, 1995 (2012).
- [30] R. Hill, *Proc. Phys. Soc. London* **65**, 349 (1952).
- [31] P. Loubeyre, R. Letoullec, D. Hausermann, M. Hanfland, R.J. Hemley, H.-K. Mao, and L. W. Finger, *Nature (London)* **383**, 702 (1996).