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CHEMISTRYNew high-pressure van der Waals compound $\text{Kr}(\text{H}_2)_4$ discovered in the krypton-hydrogen binary systemAnnette K. Kleppe¹, Mónica Amboage¹ & Andrew P. Jephcoat^{1,2*}Received
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The application of pressure to materials can reveal unexpected chemistry. Under compression, noble gases form stoichiometric van der Waals (vdW) compounds with closed-shell molecules such as hydrogen, leading to a variety of unusual structures. We have synthesised $\text{Kr}(\text{H}_2)_4$ for the first time in a diamond-anvil high-pressure cell at pressures ≥ 5.3 GPa and characterised its structural and vibrational properties to above 50 GPa. The structure of $\text{Kr}(\text{H}_2)_4$, as solved by single-crystal synchrotron X-ray diffraction, is face-centred cubic (fcc) with krypton atoms forming isolated octahedra at fcc sites. Rotationally disordered H_2 molecules occupy four different, interstitial sites, consistent with the observation of four Raman active H_2 vibrons. The discovery of $\text{Kr}(\text{H}_2)_4$ expands the range of pressure-stabilised, hydrogen-rich vdW solids, and, in comparison with the two known rare-gas- H_2 compounds, $\text{Xe}(\text{H}_2)_8$ and $\text{Ar}(\text{H}_2)_2$, reveals an increasing change in hydrogen molecular packing with increasing rare gas atomic number.

Familiar concepts of chemical bonding and interactions in molecular systems can change dramatically upon compression, and new concepts can be revealed. At gigapascal pressures the atomic rare gases (e.g., He, Ar, Xe), diatomic molecules (e.g., H_2 , N_2 , O_2) and even full-shell molecules (e.g., CH_4 , SiH_4) can interact with each other and form compounds. The first reported, pressure-stabilized, stoichiometric van der Waals (vdW) solid was reported in the He- N_2 system, $\text{He}(\text{N}_2)_{11}$ ¹. Since then a variety of stoichiometric vdW compounds have been synthesised under pressure for example, in the systems He-Ne², Ar- H_2 ³, CH_4 - H_2 ⁴, and most recently Xe- H_2 ^{5,6}. The study of hydrogen-rich binary mixtures has attracted particular attention because they are of interest to planetary science and astronomy, are potentially relevant technologically for hydrogen storage⁷, and, last but not least, offer the tantalising prospect to promote the pressure-induced insulator-metal transition in hydrogen at a lower pressure than required for pure hydrogen (e.g., 3, 8).

Two hydrogen-rich rare gas RG binary mixtures have been investigated so far: Ar- H_2 and Xe- H_2 ; and two vdW compounds have been discovered and characterised in detail: $\text{Ar}(\text{H}_2)_2$ and $\text{Xe}(\text{H}_2)_8$. $\text{Ar}(\text{H}_2)_2$ forms at 4.3 GPa and X-ray diffraction data showed $\text{Ar}(\text{H}_2)_2$ to be isostructural with the MgZn_2 Laves phase to at least 27 GPa³. The observation of a Raman active H_2 vibron confirmed the presence of molecular H_2 in the structure, and its disappearance around 175 GPa indicated the possibility of a pressure-induced molecular dissociation followed by metallization³. The prospect of metallic hydrogen stimulated extensive experimental and theoretical investigation of this molecular compound (e.g., 9–12) with the latest study in fact predicting a much higher metallization pressure for hydrogen mixed with argon than for pure hydrogen¹². Stability of $\text{Ar}(\text{H}_2)_2$ to at least 220 GPa is supported by IR spectroscopic measurements¹³.

$\text{Xe}(\text{H}_2)_8$ was found to be stable above 5.4 GPa with a hexagonal crystal structure⁵. The Xe sublattice, as determined by X-ray diffraction, consists of Xe-Xe pairs oriented along the *c* axis of the unit cell. Raman and IR spectra composed of multiple H_2 vibrons confirmed the presence of molecular hydrogen in $\text{Xe}(\text{H}_2)_8$ and support that its structure can be viewed as a tripled, solid H_2 hcp lattice modulated by layers consisting of Xe dimers⁵. IR spectra showed the $\text{Xe}(\text{H}_2)_8$ compound to remain an insulator to at least 255 GPa⁵ while its calculated metallization pressure is around 250 GPa¹⁴.

The Kr- H_2 binary system has not been investigated under compression experimentally and so the possible vdW compounds are unknown. A recent first-principles study suggested that $\text{Kr}(\text{H}_2)_2$ was a possible candidate for observing the pressure-induced metallization of hydrogen based on the similarities of $\text{RG}(\text{H}_2)_2$ to $\text{RG}(\text{He})_2$ systems¹⁵. Here we present the first high-pressure single-crystal X-ray diffraction study of a Kr- H_2 solid synthesised at pressures ≥ 5.3 GPa in the diamond-anvil cell from a mixture of 8 vol% Kr and balance H_2 (Fig. 1).

Figure 1 | Optical microscope photographs showing a $\text{Kr}(\text{H}_2)_4$ single-crystal in solid hydrogen in the diamond-anvil cell under pressure at 298 K. There is a striking visible difference in shape between the crystal of experiment 1 (a) and experiment 2 (b) (squared, sharp edges versus rounded shape). Except for a difference in their crystallographic orientation with respect to the X-ray beam the X-ray diffraction and Raman spectroscopic data match showing both crystals as well crystalline.

Complementary Raman spectroscopic measurements were performed to verify the structural environments of the hydrogen molecules determined from single-crystal X-ray diffraction data and to characterize the evolution of the H_2 molecular bond under pressure.

Results

The structure of $\text{Kr}(\text{H}_2)_4$ and its evolution under pressure. The structure of the $\text{Kr}-\text{H}_2$ compound was solved from a single-crystal data set collected at 11.24 GPa (Tab. 1, Supplementary Fig. S1 and Tab. S2). The Kr sublattice is face-centred cubic (fcc), space group $\text{Fm}-3\text{m}$, and characterised by isolated Kr octahedra occupying the fcc sites (Fig. 2). Interestingly the intra-octahedral Kr-Kr bond distances (3.35 Å at 11.24 GPa) are comparable to the Kr bond distance in the pure krypton solid at the same pressure. The inter-octahedral distances are comparably long with the shortest inter-octahedral Kr-Kr distance being 4.89 Å at 11.24 GPa. Under pressure the volume of $\text{Kr}(\text{H}_2)_4$ compresses continuously to at least 51 GPa with the longer inter-octahedral Kr-Kr distance decreasing faster than the shorter intra-octahedral distance (Fig. 3). Compression of the intra-octahedral distance follows the compressional behaviour of the Kr-Kr distance in solid krypton. Above 15 GPa the fcc Kr sublattice indicates a small tetragonal distortion (space group $\text{I}4/\text{mmm}$) deviating from the cubic unit cell by about 1% based on $c_{\text{tet}}/a\sqrt{2} = 1.01$. Cubic and tetragonal refinements of the $\text{Kr}(\text{H}_2)_4$ structure are of comparable quality to 51 GPa and for the purpose of volume determination we have refined the Kr substructure with cubic symmetry.

Table 1 | Details of the structural refinement of $\text{Kr}(\text{H}_2)_4$ at 11.24 GPa and 298 K

Crystal system	cubic
Space group	$\text{Fm}-3\text{m}$
Lattice parameter (Å)	$a = 11.663(1)$
Volume (Å ³)	1586.43(3)
Z	24
Reflections collected	781
Unique reflections ($>4\sigma$)	127 (117)
R_{int} (%)	3.51
R_{sigma} (%)	1.68
R_1 (observed data) (%)	1.63
R_1 (all data) (%)	1.91
wR_2 (%)	3.75
Goodness-of-fit	1.191

Figure 2 | Face-centered cubic structure of $\text{Kr}(\text{H}_2)_4$ at 11.24 GPa. Isolated krypton octahedra (green) are located at each lattice point. Grey spheres represent rotationally disordered hydrogen molecules.

The low X-ray scattering cross-section of hydrogen, the contrast with heavier elements, and the micron-sized sample in the diamond-anvil cell pose a major challenge in high-pressure X-ray diffraction experiments on hydrogen-rich samples for the determination of H_2 positions. In addition, single-crystals become increasingly strained under pressure and the reflection rocking curve deteriorates. Our structural model of $\text{Kr}(\text{H}_2)_4$ could be completed by locating the hydrogen molecules using difference-Fourier maps. The H_2 positions were identified at four different interstitial sites (Tab. 2) appearing with peak scattering densities from 0.9 to 1.23 $\text{e}\text{\AA}^{-3}$ in the $F_{\text{calc}}-F_{\text{obs}}$ difference electron density maps. Including the H_2 molecules in the refinement improved the refinement quality factor R_1 by 1.2% compared to a model with Kr atoms only. Further, the number of H_2 molecules refined confirms the stoichiometry $\text{Kr}(\text{H}_2)_4$ which was initially (with only the Kr substructure established) derived from volume considerations based on the separate equation of states of pure krypton¹⁶ and hydrogen¹⁷.

High-pressure Raman spectra and the H_2 sublattice of $\text{Kr}(\text{H}_2)_4$. The Raman spectra of $\text{Kr}(\text{H}_2)_4$ are characterised by roton peaks between 200–1200 cm^{-1} and by a maximum of four H_2 vibrons between 4200–4500 cm^{-1} confirming the presence of molecular hydrogen in the structure (Fig. 4, 5). The roton frequencies cannot be distinguished from those of pure hydrogen at the same pressure indicating rotational disorder of the H_2 molecules. The four H_2 vibrons are observed at higher frequencies than the $\text{Q}_1(1)$ vibron of solid H_2 at the same pressure. Attributing these vibrons to H_2 molecules in four different crystallographic sites is consistent with the four H_2 sites determined from the difference-Fourier maps.

Under compression the vibrons shift continuously to higher frequencies (Fig. 6) confirming the persistence of molecular H_2 and the absence of a major structural change in $\text{Kr}(\text{H}_2)_4$ to at least 51 GPa in agreement with the continuous volume compression. The two lower frequency vibrons (ν_1, ν_2) remain intense to the highest pressure, the higher frequency vibron ν_3 weakens significantly, and the fourth vibron, ν_4 , is very weak and not uniformly observed across the pressure range studied. Interestingly, the two H_2 vibrons, ν_1 and ν_2 , show a striking reversal in their relative intensities under pressure: ν_1 loses intensity while ν_2 gains intensity. Around 15 GPa ν_1 and ν_2

Figure 3 | Compressional behaviour of the $\text{Kr}(\text{H}_2)_4$ structure. (a) Pressure-volume data. A Vinet equation of state (EoS) fitted to the data with $V_0 = 5237.952 \text{ \AA}^3$ gives $B_0 = 0.18(3) \text{ GPa}$ and $B' = 7.7(2)$. The fixed V_0 value is based on the equivalent volumes of pure, solid krypton and hydrogen. (b) Intra- and shortest inter-octahedral Kr-Kr distances as function of pressure. For comparison Kr-Kr distances in the pure krypton solid (16) are given in the inset. Solid lines are guides to the eye.

are of equal intensity, and above about 30 GPa their intensity ratio is constant. The changeover in dominant intensity from v_1 to v_2 occurs at the pressure above which a tetragonal distortion is detectable in the fcc Kr sublattice. Such coincidence suggests that the change in relative intensity of the H_2 vibrons can be associated with a change in the H_2 sublattice which in turn subtly affects the Kr sublattice at pressures $>15 \text{ GPa}$. We can exclude a re-distribution of H_2 molecules between two different crystallographic sites because all four hydrogen sites are fully occupied.

Discussion

In order to provide additional insight and to enable a more systematic understanding of weakly-bonded systems under pressure we compare $\text{Kr}(\text{H}_2)_4$ with the two, other known RG- H_2 compounds, $\text{Xe}(\text{H}_2)_8$ and $\text{Ar}(\text{H}_2)_2$.

From the RG sublattice point of view a common characteristic of $\text{Kr}(\text{H}_2)_4$, $\text{Xe}(\text{H}_2)_8$ and $\text{Ar}(\text{H}_2)_2$ is that the smallest RG-RG distance is comparable to the next nearest-neighbour distances in the pure RG solid at the same pressure. While $\text{Ar}(\text{H}_2)_2$ features only Ar-Ar distances close to those in solid Ar at the same pressure, $\text{Kr}(\text{H}_2)_4$ and

$\text{Xe}(\text{H}_2)_8$ show a striking difference: Two different sets of atomic distances occur: intra- and inter-atomic RG-RG distances with the intra-atomic distances being comparable to the next nearest-neighbour distances in the pure RG solid at the same pressure. For $\text{Kr}(\text{H}_2)_4$ the intra-octahedral Kr-Kr distances are comparable to the Kr-Kr distances in solid krypton, and for $\text{Xe}(\text{H}_2)_8$ the Xe-Xe dimer separation was reported to match the Xe-Xe distance in solid xenon⁵.

Further, the pressure dependence of the intra-octahedral Kr-Kr distance follows closely that of the Kr-Kr distance in solid krypton making the Kr-octahedra appear as detached units, neither interacting with each other nor with the H_2 sublattice. A similar observation applied to the Xe-dimers in $\text{Xe}(\text{H}_2)_8$ ⁵. However, clearly compound formation and stability is a complex process dominated by a subtle interplay of van der Waals and weak covalent forces or possibly charge transfer interactions as argued for in $\text{Xe}(\text{H}_2)_8$ ^{5,14}.

The hydrogen-lattice vibrational properties of $\text{Kr}(\text{H}_2)_4$, $\text{Xe}(\text{H}_2)_8$ and $\text{Ar}(\text{H}_2)_2$ show strong similarities to solid H_2 . The rotational vibrations of all compounds are reported as indistinguishable from those of solid hydrogen indicating freely rotating H_2 molecules. The observation of multiple vibrons for $\text{Xe}(\text{H}_2)_8$ and $\text{Kr}(\text{H}_2)_4$ contrasts

Table 2 | Refined atomic coordinates and displacement parameters for $\text{Kr}(\text{H}_2)_4$ at 11.24 GPa and 298 K

Atom	Wyckoff position	x	y	z	U_{11}	U_{22}	U_{33}	U_{eq}
Kr	24e	0.20325(4)	0	0	0.0212(3)	0.0176(2)	0.0176(2)	0.0188(2)
H1	4b	0.5	0	0				
H2	32f	0.384(2)	0.384(2)	0.384(2)				
H3	24d	0	0.25	0.25				
H4	32f	0.172(2)	0.172(2)	0.172(2)

Figure 4 | Raman spectrum of $\text{Kr}(\text{H}_2)_4$ at a selected pressure of 19.6 GPa; background has not been subtracted. Roton peaks are observed in the low frequency range and two vibrons, v_1 and v_2 , in the high-frequency range. The other two, much weaker vibrons, v_3 and v_4 , are not observed at this pressure. The rotons and $Q_1(1)$ vibron frequency of solid H_2 at the same pressure are indicated by cyan, dotted lines.

with solid H_2 . The origin of the vibron multiplet structure for $\text{Xe}(\text{H}_2)_8$ has been explained with H_2 forming a sublattice that is a $3 \times 3 \times 3$ superstructure of the hcp lattice of solid hydrogen⁵. The Raman spectrum of $\text{Kr}(\text{H}_2)_4$ reveals four H_2 vibrons that can be attributed to hydrogen molecules in four different crystallographic sites. Three H_2 vibrons are expected for $\text{Ar}(\text{H}_2)_2$ based on group theoretical arguments¹⁰ but only a single vibron has been measured with the other two being thought to be too weak to be observed.

The H_2 vibrons in the RG- H_2 compounds increase under compression as is expected from increasing repulsion between molecules. An interesting, well studied characteristic of the vibron in solid hydrogen is its turnover around 35 GPa above which its frequency decreases monotonically. This behaviour has been attributed to vibrational coupling between H_2 molecules; pressure-induced bond weakening does not occur until over 145 GPa¹⁸. We observe that the intense H_2 Raman vibron of $\text{Xe}(\text{H}_2)_8$ mirrors the behaviour of the vibron in solid hydrogen turning over around 40 GPa (inset Fig. 6). Starting from a lower frequency, it crosses the pressure-frequency trajectory of the pure hydrogen vibron at about 50 GPa and remains at a higher frequency to at least 142 GPa. The intense H_2 vibron we observe in $\text{Xe}(\text{H}_2)_8$ is the only vibron of the RG- H_2 compounds reported so far that on compound formation and at pressures <50 GPa exhibits a frequency lower than the vibron of pure hydrogen at the same pressure.

The H_2 vibrons of $\text{Kr}(\text{H}_2)_4$ and the single vibron of $\text{Ar}(\text{H}_2)_2$ are initially higher than the vibron of pure H_2 and harden continuously under compression over the investigated pressure range with the v_1 vibron of $\text{Kr}(\text{H}_2)_4$ appearing to flatten around 40–50 GPa so likely turning over at higher pressures. Continuously increasing H_2 Raman vibron frequencies have also been observed for H_2 dissolved in rare-gas matrices where there is no possibility of vibrational coupling due to mismatch of vibrational frequencies between matrix and H_2 molecules¹⁹. The RG- H_2 compounds appear therefore to show “composite” behaviour, with some of the H_2 vibrational properties dominated by H_2 - H_2 intermolecular interactions of near by H_2 and some more strongly modified by nearby RG structural units.

Details of the electronic band structure of $\text{Kr}(\text{H}_2)_4$ and the possibility of metallization present a challenge for future experimental and theoretical studies; experimental IR data in the megabar range would be particularly valuable. Furthermore, the low-pressure phase diagram of the Kr- H_2 binary system is unexplored and there may be other stoichiometries stabilized for different starting mixtures.

Figure 5 | Raman spectra of $\text{Kr}(\text{H}_2)_4$ (black) and the surrounding, solid H_2 (cyan) as a function of pressure at 298 K. Spectra are normalised to the most intense vibron and offset for clarity. Background due to fluorescence of the diamond anvils has been subtracted.

Methods

Diamond-anvil cell sample loading and crystal synthesis. In two separate experiments a single-crystal of $\text{Kr}(\text{H}_2)_4$ was grown in a diamond-anvil cell (DAC) from a pre-mixed gas of composition 8 vol% Kr and 92 vol% H_2 (certified accuracy $\pm 2\%$ from Air Liquide). In both runs a DAC equipped with 0.3 mm culet diamonds and an opening angle of 76 deg (Betsa, France) was used. A Re gasket pre-indented to 25 μm thickness with a hole of 120 μm diameter formed the sample chamber and a ruby sphere served as pressure calibrant²⁰. The pre-mixed Kr- H_2 gas was loaded in the DAC at 0.2 GPa²¹. Kr and H_2 are miscible in the liquid phase. By increasing the pressure delicately a crystal was grown from the mixture at a pressure ≥ 5.3 GPa. At slightly higher-pressure, ~ 5.5 GPa, solidification of the excess liquid was observed. 5.5 GPa is the known solidification pressure for pure hydrogen (e.g., 22, 23), and Raman spectroscopic measurements confirmed the solidified excess liquid as solid hydrogen. For the high-pressure experiment hydrogen acts as a pressure-transmitting medium and ensures quasi-hydrostatic conditions up to the highest pressures reached in these experiments; 26.7 GPa in experiment 1 and 50.9 GPa in experiment 2. We cannot exclude the possibility that the starting stoichiometry was changed due to hydrogen dissolving into the gasket material under compression²⁴. A possible loss of H_2 to the Re gasket would affect the total amount of pure hydrogen in the sample chamber but not the formation of the observed Kr- H_2 compound because this compound was grown in the presence of excess hydrogen and is in equilibrium with pure, solid H_2 at pressures ≥ 5.5 GPa.

Single-crystal X-ray diffraction. Single-crystal diffraction data have been collected on beamline I15 at Diamond Light Source (UK). The diffraction experiments were performed with a monochromatic beam ($\lambda = 0.3647$ Å) collimated by a tungsten pinhole down to 20 μm in diameter. A MAR345 image plate (MarResearch) was used as a detector with sample-to-detector distances between 250 and 270 mm. The DAC,

Figure 6 | Pressure dependence of the H_2 vibrons of $Kr(H_2)_4$ and surrounding solid H_2 (cyan). Errors in frequency and pressure are within the size of the symbol. The data is well represented with 2nd and 3rd order polynomials (Supplementary Tab. S3). The pressure dependence of the vibron of solid hydrogen agrees well with literature values (dotted grey line²²; solid grey line²³). The pressure dependence of the vibron of $Ar(H_2)_2$ ¹⁰ and the most intense vibron of $Xe(H_2)_8$ are given for comparison. The latter matches the data by Somayazulu et al. (2010). The inset shows the pressure dependence of the most intense $Xe(H_2)_8$ vibron and the $Q_1(1)$ vibron from the surrounding, bulk H_2 zoomed out to 142 GPa.

positioned on a 6-circle Newport diffractometer with kappa geometry, could be rotated around the ϕ -axis, and data sets were collected using ϕ -scans over 60 and 73 deg, step sizes between 0.5 and 2 deg, and exposure times of 0.25 to 4.0 sec per step. The data were processed using CrysAlis^{Pro} software (Agilent Technologies) and the WinGX version of SHELXS and SHELXL²⁵.

Raman spectroscopy. Unpolarized Raman spectra have been recorded from the $Kr-H_2$ single-crystal and the excess, solid H_2 in 180° back-scattering geometry over the range 3800–4800 cm^{-1} (region of the H_2 vibron) with spot tests in the range 200–1200 cm^{-1} (region of the H_2 rotors). The instrument used was the Labram HR800 (Horiba Jobin Yvon) at beamline I15, Diamond Light Source (UK). It was equipped with 1200 g grating and an air cooled CCD detector. The spectra were excited by the 473 nm line of a 50 mW Cobalt Blues TM laser focused down to a 10 μm spot on the sample and collected through a 50 μm confocal aperture. The intrinsic resolution of the spectrometer is $<1.0 cm^{-1}$ and calibrations are accurate to $\pm 1 cm^{-1}$. The frequency of each Raman band was obtained by Voigtian curve fitting using a least-squares algorithm. In experiment 1 some spectra collected on the $Kr(H_2)_4$ and H_2 crystal each contained weak contributions from the other solid phase due to the small sample size but deconvolution was readily done.

The Raman spectroscopic data of $Xe(H_2)_8$ to 142 GPa were measured in 135 deg scattering geometry with a SPEX Triplemate equipped with a back-illuminated

liquid- N_2 -cooled CCD detector at the Department of Earth Sciences, University of Oxford, UK. The spectra were excited by the 514.5 or 488-nm line of an argon-ion laser focused to a $\leq 10 \mu m$ spot on the sample and collected through an adjustable confocal aperture closed down to about 10 μm in diameter >90 GPa. The intrinsic resolution of the spectrometer is $1.5 cm^{-1}$ and calibrations are accurate to $\pm 1 cm^{-1}$.

- Vos, W. L. *et al.* A high-pressure van der Waals compound in solid nitrogen-helium mixtures. *Nature* **358**, 46–48 (1992).
- Loubeyre, P., Jean-Louis, M. & LeToullec, R. High pressure measurements of the He-Ne binary phase diagram at 296 K: Evidence for the stability of a stoichiometric $Ne(He)_2$ solid. *Phys. Rev. Lett.* **70**, 178–181 (1993).
- Loubeyre, P., LeToullec, R. & Pinceaux, J. P. Compression of $Ar(H_2)_2$ up to 175 GPa: A new path for the dissociation of molecular hydrogen? *Phys. Rev. Lett.* **72**, 1360–1363 (1994).
- Somayazulu, M., Finger, L. W., Hemley, R. J. & Mao, H.-K. High-pressure compounds in methane-hydrogen mixtures. *Science* **271**, 1400–1402 (1996).
- Somayazulu, M. *et al.* Pressure-induced bonding and compound formation in xenon-hydrogen solids. *Nat. Chem.* **2**, 50–53 (2010).
- Jephcoat, A. P., Amboage, M. & Kleppe, A. K. Structural and vibrational properties of condensed phases in xenon molecular binary systems: He-Xe, H_2 -Xe. *J. Phys. Conf. Ser.* **215**, 012016 (2010).
- Mao, L. W. & Mao, H.-K. Hydrogen storage in molecular compounds. *Proc. Natl. Acad. Sci.* **101**, 708–710 (2004).
- Strobel, T. A., Somayazulu, M. & Hemley, R. J. Novel pressure-induced interactions in silane-hydrogen. *Phys. Rev. Lett.* **103**, 065701 (2009).
- Bernard, S., Loubeyre, P. & Zerah, G. Phase transition in $Ar(H_2)_2$: a prediction of metallic hydrogen organized in lamellar structures. *Europhys. Lett.* **37**, 477–482 (1997).
- Ulivi, L., Bini, R., Loubeyre, P., LeToullec, R. & Jodl, H. J. Spectroscopic studies of the $Ar(H_2)_2$ compound crystal at high pressure and low temperatures. *Phys. Rev. B* **60**, 6502–6512 (1999).
- Cazorla, C. & Errandonea, D. *Ab initio* study of compressed $Ar(H_2)_2$: Structural stability and anomalous melting. *Phys. Rev. B* **81**, 104108 (2010).
- Yao, Y. & Klug, D. D. High-pressure phase transition and metallization in $Ar(H_2)_2$. *Phys. Rev. B* **83**, 020105 (2011).
- Hemley, R. J. Effects of high pressure on molecules. *Annu. Rev. Phys. Chem.* **51**, 763–800 (2000).
- Kaewmaraya, T. *et al.* Theoretical investigation of xenon-hydrogen solids under pressure using *ab initio* DFT and GW calculations. *Phys. Rev. B* **84**, 092101 (2011).
- Cazorla, C., Errandonea, D. & Sola, E. High-pressure phases, vibrational properties, and electronic structure of $Ne(He)_2$ and $Ar(He)_2$: A first-principles study. *Phys. Rev. B* **80**, 064105 (2009).
- Errandonea, D., Schwager, B., Boehler, R. & Ross, M. Phase behaviour of krypton and xenon to 50 GPa. *Phys. Rev. B* **65**, 214110 (2002).
- Loubeyre, P. *et al.* X-ray diffraction and equation of state of hydrogen at megabar pressures. *Nature* **383**, 702–704 (1996).
- Mao, H.-K. & Hemley, R. J. Ultrahigh-pressure transitions in solid hydrogen. *Rev. Mod. Phys.* **66**, 671–692 (1994).
- Loubeyre, P., Toullec, R. & Pinceaux, J. P. Raman measurements of the vibrational properties of H_2 as a guest molecule in dense helium, neon, argon, and deuterium systems up to 40 GPa. *Phys. Rev. B* **45**, 12844–12853 (1992).
- Mao, H.-K., Xu, J. & Bell, P. Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions. *J. Geophys. Res.* **91**, 4673–4676 (1986).
- Jephcoat, A. P., Mao, H.-K. & Bell, P. M. in *Hydrothermal Experimental Techniques*, eds Ulmer, G. C. & Barnes, H. L. (Wiley-Interscience, New York), 469–506 (1987).
- Mao, H.-K., Bell, P. M. & Hemley, R. J. Ultrahigh Pressures: Optical Observations and Raman Measurements of Hydrogen and Deuterium to 1.47 Mbar. *Phys. Rev. Lett.* **55**, 99–102 (1985).
- Sharma, S. K., Mao, H.-K. & Bell, P. M. Raman measurements of hydrogen in the pressure range 0.2–630 kbar at room temperature. *Phys. Rev. Lett.* **44**, 886–888 (1980).
- Atou, T. & Badding, J. V. *In situ* diffraction study of the formation of rhenium hydride at high pressure. *J. Solid State Chem.* **118**, 299–302 (1995).
- Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr. A* **64**, 112–122 (2008).

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Author contributions

A.K.K., A.P.J. and M.A. designed the research; A.K.K., A.P.J. and M.A. performed research; A.K.K. and M.A. analysed data, and A.K.K. and A.P.J. wrote the paper.

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