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Superconductivity in La and Y hydrides: Remaining questions to experiment and theory

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ABSTRACT

Recent reports of the superconductivity in hydrides of two different families (covalent lattice, as in SH_3 and clathrate-type H-cages containing La and Y atoms, as in LaH_{10} and YH_6) have revealed new families of high-T_c materials with T_c's near room temperature values. These findings confirm earlier expectations that hydrides may have very high T_c's due to the fact that light H atoms have very high vibrational frequencies, leading to high T_c values within the conventional Bardeen–Cooper–Schrieffer phonon mechanism of superconductivity. However, as is pointed out by Ashcroft, it is important to have the metallic hydrogen "alloyed" with the elements added to it. This concept of a metallic alloy containing a high concentration of metal-like hydrogen atoms has been instrumental in finding new high-T_c superhydrides. These new superhydride "room-temperature" superconductors are stabilized only at very high pressures above 100 GPa, making the experimental search for their superconducting properties very difficult. We will review the current experimental and theoretical results for LaH_{10-x} and YH_{6-x} superhydrides.

I. INTRODUCTION

The attainment of room-temperature superconductivity is a long-standing challenge related historically to the metallic phase of hydrogen.[1–3] The ambient-pressure molecular crystals of hydrogen are stable only at low temperature, and a metallic atomic-like hydrogen phase was proposed by Wigner and Huntington to occur under high pressure conditions.[4] The pressure of metallization, estimated by Wigner and Huntington, of about 20 GPa, ultimately proved to be incorrect, and it was realized later that the actual metallization pressure should be around 500 GPa.[5] Metallic hydrogen is also predicted to have a very high superconducting T_c,[6] which naturally arises from the Bardeen–Cooper–Schrieffer (BCS)[7] electron-phonon coupling mechanism involving hydrogen's high vibrational frequencies. The atomic metallic phase of hydrogen is claimed to have been produced in several reports, including recently by Dias and Silvera,[8] but all of these claims have met serious criticism.[9–12] None of these reports have been able to show measurement of superconductivity in the claimed metallic phase.

After the BCS mechanism was established,[7] it became clear that high vibrational frequencies are conducive to high T_c values. Many researchers have focused on studying the superconductivity of metallic hydrides in the hope of increasing T_c due to involvement of hydrogen vibrations in the "superconducting glue" provided by the electron-phonon mechanism. However, in many attempts to find such hydrides, T_c's have failed to exceed 20 K.[13] The formed hydrides did not have hydrogen-related electronic states at the Fermi level of the hydride. The chemical nature of hydrogen bonding in materials (ionic, covalent, or more exotic multicenter bonds) has prevented hydrogen electronic states from residing at the position of the Fermi level in all studied ambient-pressure hydrides.

However, attempts to find superconducting hydrides have produced another idea involving the concept of "doped" metallic hydrogen,

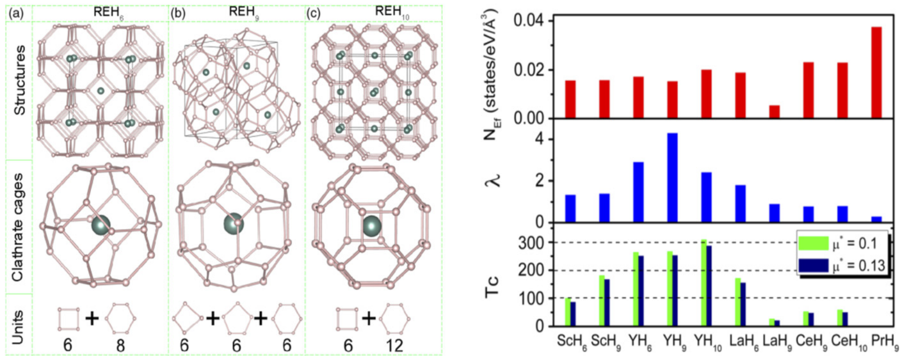

FIG. 1. Clathrate structures of typical metal superhydrides (polyhydrides).[21] Maximum T_c is predicted for YH_{10} and is slightly above room temperature at 250 GPa. [Reprinted Figs. 2 and 4 with permission from Peng *et al.*, Phys. Rev. Lett. **119**(10), 107001 (2017). Copyright (2017) The American Physical Society.]

which is usually attributed to Gilman and Ashcroft.[14–16] Originally, Ashcroft conjectured that certain compounds of hydrogen with other elements in the periodic table may form metallic alloys, or, in other words, sustain a metallic hydrogen sublattice doped with well selected elements. Such "doped" compounds of hydrogen may have a stability range at pressures much lower than the 500 GPa required to stabilize pure atomic metallic hydrogen.[5] These conditions may be amenable to the experimental techniques we currently possess for measuring the superconducting response at high pressures. While Ashcroft's idea did not work well for the compounds he proposed (silane, SiH_4[17] and similar group IV hydrides), more recent predictions by Li *et al.*[18] have stimulated experimental work by Drozdov *et al.*[19] and theoretical work by Duan *et al.*,[20] which found high T_c superconductivity in H_3S below 200 GPa at $T_c \sim 200$ K. These papers were an incentive for predicting high T_c's in many unusual hydrides stabilized in high pressure environments.

The highest T_c values have been predicted so far for compounds of La and Y: LaH_{10} and YH_{10},[21,22] and recently in Li_2MgH_{16},[23] with a predicted value $T_c \sim 473$ K at 250 GPa. These compounds have very interesting clathrate-like caged networks of hydrogen atoms with metal atoms embedded in such clathrate cages. Indeed, the LaH_{10} "superhydride" was discovered very soon after its prediction by Geballe *et al.*,[24] and very high T_c values in this compound were reported recently by Somayazulu *et al.* (260–280 K)[25] and Drozdov *et al.* (254 K).[26] With these findings, we are entering an era of room-temperature superconductivity, albeit under very high-pressure conditions (above 100–150 GPa). We will provide below a summary of mostly experimental and relevant theoretically predicted properties of these new superconducting materials (LaH_{10}, YH_6, ThH_{10}) and introduce new experimental results from magnetic susceptibility studies at high pressures in LaH_{10}. For more extensive reviews on superhydrides and conventional hydrides, we redirect the reader to other sources.[13,16,27–29]

II. OVERVIEW OF THEORETICAL AND EXPERIMENTAL DATA FOR LaH_{10}

As with all superhydrides measured so far, theoretical predictions come first. For example, the theoretical predictions of T_c in clathrate-like structured hydrides were published as early as 2012 for CaH_6.[30] The proposed structure was sodalite-like CaH_6, with a predicted T_c value of around 230 K.[30] However, the relation of this structure to the clathrate-like caged family of superhydrides (several structural units are shown in Fig. 1) was realized later after publications by Peng *et al.*[21] and Liu *et al.*,[22] which predicted high T_c values approaching or exceeding room temperature in LaH_{10} and YH_{10} superhydrides. The predicted T_c values in selected metal hydrides from Peng *et al.*[21] are shown in Fig. 2. Liu *et al.*[22] predicted T_c's of around 280 K in LaH_{10} around 210 GPa, and around 315 K in YH_{10} at 250 GPa (see Fig. 2).

The experimental confirmation of an Fm-3mLaH_{10} structure quickly followed in the publication by Geballe *et al.*[24] The material was produced by heating an La flake in a hydrogen pressure medium at about 170 GPa. It was found that LaH_{10} Fm-3m structure is stabilized above 170 GPa, see Fig. 3, and at pressures below ~165 GPa; the stable structure is R-3m LaH_{10}. This finding supports theoretical estimates regarding the dynamic instability of LaH_{10} below 200 GPa,[16,31] albeit the experimental pressure for the stability range of Fm-3m structure being significantly lower (165 GPa) than theoretical estimates.

The first reports of superconductivity in LaH_{10} appeared as arXiv publications. Drozdov *et al.* submitted a brief report of a resistivity drop at ~215 K in laser-heated samples loaded in a hydrogen pressure

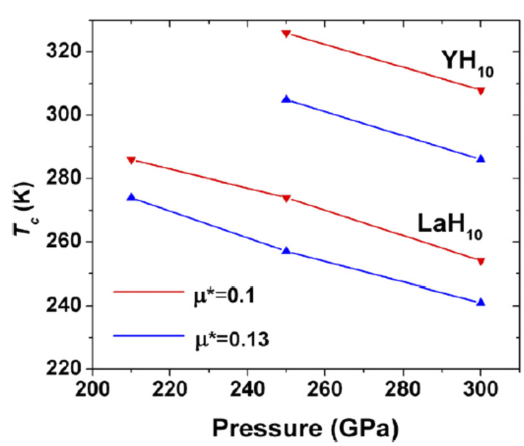

FIG. 2. Predicted superconductivity in LaH_{10} and YH_{10} superhydrides.[22] Blue and red curves and symbols correspond to the indicated values of the Morel–Anderson pseudopotential, μ*.

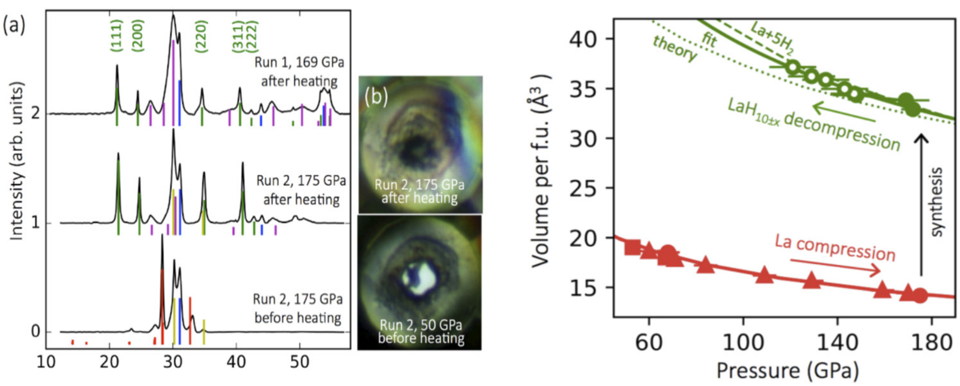

FIG. 3. X-ray diffraction of LaH_{10} sample after laser heating at 175 GPa and 169 GPa.[24] Right panel: Volume per formula unit compared with theory and sum of the volumes of pure La and five H_2 units. [Reproduced with permission from Geballe *et al.*, Angew. Chem., Int. Ed. **57**, 688–692 (2018). Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.]

medium.[32] No structural data were given to support the claimed LaH_{10} superconducting phase. Shortly after, Somayazulu *et al.* submitted an arXiv contribution on the superconductivity of the LaH_{10} phase, which was confirmed by x-ray diffraction studies, with the onset of T_c up to 280 K.[33] The four-probe data with zero residual resistance demonstrated a T_c onset at about 260 K. These results are in Ref. 25 along with additional measurements probing critical currents in the samples.

Drozdov *et al.* published another arXiv paper, claiming LaH_{10} with a maximum T_c of about 254 K,[34] confirmed by an x-ray derived LaH_{10} structure, measured magnetic field suppression of T_c, and the effect of Deuterium-doping on T_c. These results are in Ref. 26.

The experimental setting for resistivity measurements using the four-probe technique from Somayazulu *et al.*[25] is shown in Fig. 4. The sample of La was embedded in an ammonia borane pressure medium and pressed against four contacts on one of the diamond anvils. The sample was heated by laser under high pressure conditions from the side opposite to the electrodes, and ammonia borane served as a hydrogen source. The formation of an LaH_{10} phase was confirmed by x-ray diffraction data (Fig. 5). It was found that the onset of T_c can be observed in the temperature range of 245 K to almost 280 K in different samples, with varying hydrogen content (close to LaH_{10} as estimated from x-ray unit cell volume data; see Fig. 5).

Drozdov *et al.*[26] have published resistivity data for several samples synthesized in a hydrogen pressure medium. While the

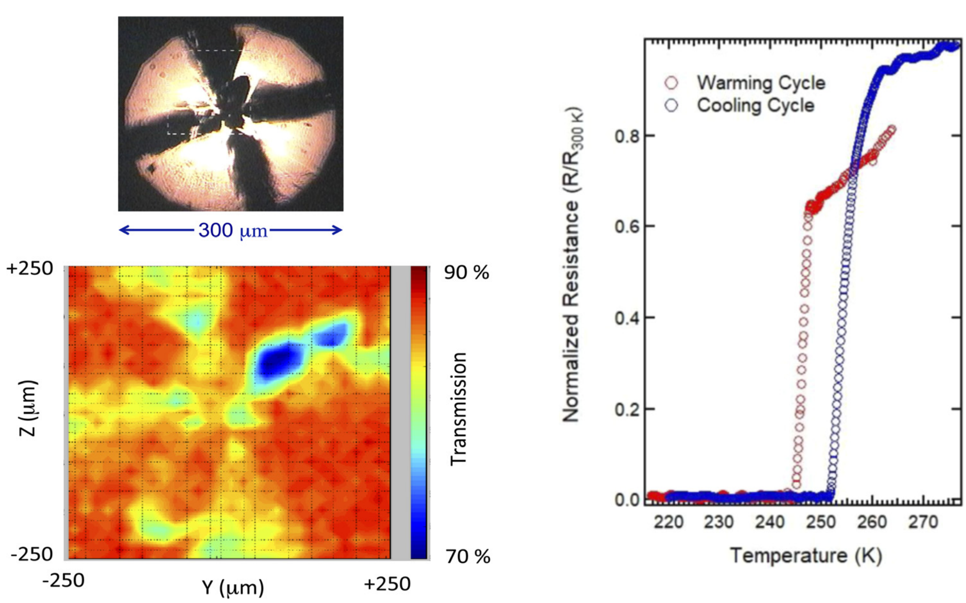

FIG. 4. Resistivity studies of superconductivity in LaH_{10}.[25] Left panel: Typical arrangement of electrical contacts and x-ray transmission scan through the sample and contact area. Right panel: Resistivity signatures of superconductivity in LaH_{10}. [Reprinted Figs. S1 and 2 with permission from Somayazulu *et al.*, Phys. Rev. Lett. **122**(2), 027001 (2019). Copyright 2019 The American Physical Society.]

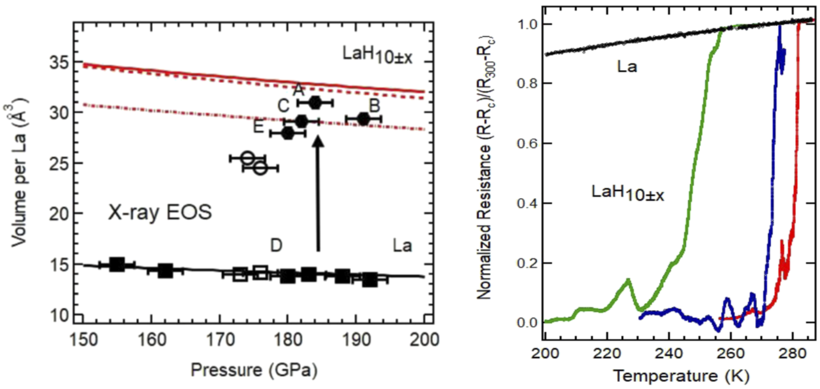

FIG. 5. Observed volumes per formula unit before and after the conversion from La to $LaH_{10\pm x}$ for several samples probed by resistivity technique.[25] The predicted P–V curves for the assemblages La + 5H2 and La + 4H2 are plotted as the dashed and dash-dot lines (respectively). Samples which do not show evidence of the conductivity drop above 80 K lie below the La + $4H_2$ line. Right panel shows the resistivity of one of the samples under varying pressure during thermal cycling (supplementary material in Ref. 25). [Reprinted Figs. S3 and S4 with permission from Somayazulu *et al.*, Phys. Rev. Lett. **122**(2), 027001 (2019). Copyright 2019 The American Physical Society.]

detailed procedure for sample synthesis is not clear from their work, it was stated that the La sample was bridged between the diamond anvils to ensure that the electrical contacts between the sample and the deposited electrodes was secured; this made sample synthesis by laser heating a challenging procedure due to an effective heat sink provided by the contacts of the samples with diamond anvils. Thus, we may assume that these synthesis conditions are not favorable for creating a relatively homogeneous, single phase of an La hydride. Indeed, the resistive response and x-ray data show the existence of multiple phases with varying hydrogen content in the reported experiments.[26]

For the LaH_{10} phase, Drozdov *et al.*[26] reported a dome-like dependence of T_c on pressure. While their measurement range extended as low as 140 GPa, they did not show any evidence of an R-3m LaH_{10} phase, which was reported by Geballe *et al.*[24] below 165 GPa—Fig. 6. This discrepancy is not clear, since both studies used La in a hydrogen pressure medium and the reported conditions for the synthesis of LaH_{10} were very similar.

Magnetic susceptibility measurements have not been attempted for LaH_{10} due to the very small volume of the synthesized samples—see Ref. 26, which is well below the limit of the MPMS squid

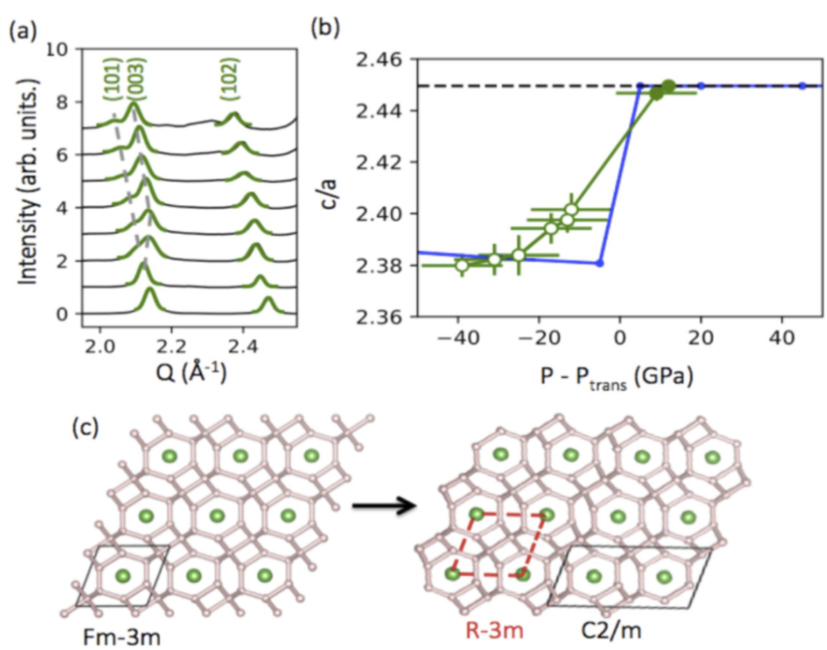

FIG. 6. Transition to a lower symmetry phase (R-3m) in LaH_{10} on decompression from ~170 GPa.[24] [Reproduced with permission from Geballe *et al.*, Angew. Chem., Int. Ed. **57**, 688–692 (2018). Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.]

system used to prove superconductivity in H_3S samples.[19] We have recently studied magnetic susceptibility in LaH_{10} using our sensitive magnetic susceptibility technique[35] and have obtained interesting initial results which we describe below.

III. MAGNETIC SUSCEPTIBILITY STUDIES AT HIGH PRESSURE IN LaH_{10}

The technique we use for magnetic susceptibility measurements is a double-modulation technique introduced originally by Timofeev,[36] which we improved[35] and adopted for measuring small samples in multimegabar experiments.[37,38] The technique is demonstrated in Fig. 7, along with the calculated and measured response from a $YBa_2Cu_3O_{7-x}$ superconductor (see Ref. 38 for details). For tiny samples the background issues become quite severe, and the diamond anvil cell, the gasket, and all surrounding metal parts should be made from nonmagnetic materials. The background signal may become comparable to the detected signal, as was the case in experiments on pure sulfur in pressures up to 230 GPa.[38] For the experiments on LaH_{10} we used a BeCu piston-cylinder, Mao-Bell type cell with a nonmagnetic NiCrAl (Russian alloy) gasket,[38] and ammonia borane as a pressure medium. The samples were handled in an inert environment to avoid contamination. The details of the loading procedure are similar to those in Ref. 25. The samples were brought to a synchrotron (Advanced Photon Source, Argonne National Laboratory, GSECARS beamline) and the La sample was heated by a pulsed laser in an ammonia borane pressure medium at about 165 GPa producing LaH_{10} samples. The details of sample synthesis are reported elsewhere.[39] The DAC with synthesized samples was brought to the HPSTAR facility in Shanghai for magnetic susceptibility measurement, and after three weeks to the Geophysical Laboratory (Carnegie Institution of Washington) for a similar set of measurements.

We were able to detect a measurable signal, however, the estimated sample size proved to be very small. We show raw data at several pressures in Fig. 8. The onset of the superconducting response was at about 250 K in two temperature scans immediately following synthesis at the beamline. After three weeks the shape of the signal changed, showing the shift in response to 278 K. This occurred without further laser heating and may be attributed to pressure effects, since average sample pressure increased to nearly 180 GPa, as measured by the shift in the edge of the Raman signal from the diamond anvils.

We have estimated sample size using previous measurements from larger samples of high-T_c superconductors and MgB_2 samples (Fig. 9). For the observed signal at 180 GPa, we obtain a sample volume of about 4×10^{-10} cm^{-3}, which corresponds to a sample size of around 10 μm in diameter, depending on the sample shape and demagnetization factor. This sample size is comparable to the size of the hot spot during the laser heating procedure. The change in T_c after synthesis may be explained by the pressure increase and/or phase changes in the sample. It should be noted that the magnetic response in Fig. 8 does not look like the expected single crystal signal shape in Fig. 7 and should correspond both to the inhomogeneity in the samples due to pressure gradients (experimentally, gradients up to 20 GPa are observed over the culet area) and to the possible presence of multiple phases. Further experiments are required to produce larger and more homogeneous samples to understand the reason for the higher T_c values observed in our experiments. However, there may be a physical reason for the higher T_c's in the LaH_{10} samples in a certain pressure range. We address this issue below.

We summarize the available experimental data for LaH_{10} samples in Fig. 10. The most interesting fact is the T_c values up to 280 K observed in experiments by Somayazulu *et al.*,[25] and in our magnetic susceptibility data. Both these studies used an ammonia borane pressure medium as a hydrogen source, and the discrepancy with Drozdov *et al.*[26] may be due to the incorporation of B or N in the synthesized samples, or to the formation of LaH_x phases different from the LaH_{10} phase. However, the x-ray data from Ref. 25 are not compatible with this explanation. A second possibility becomes evident if we notice that from theoretical results, the LaH_{10} phase is dynamically unstable below 200 GPa,[16,31] and, according to experimental data, LaH_{10} does have a phase transition to the R-3m phase below 165 GPa[24] (Fig. 6).

Indeed, the existence of a phase transition in the 160–170 GPa pressure range, which is driven by a soft mode (dynamical instability),

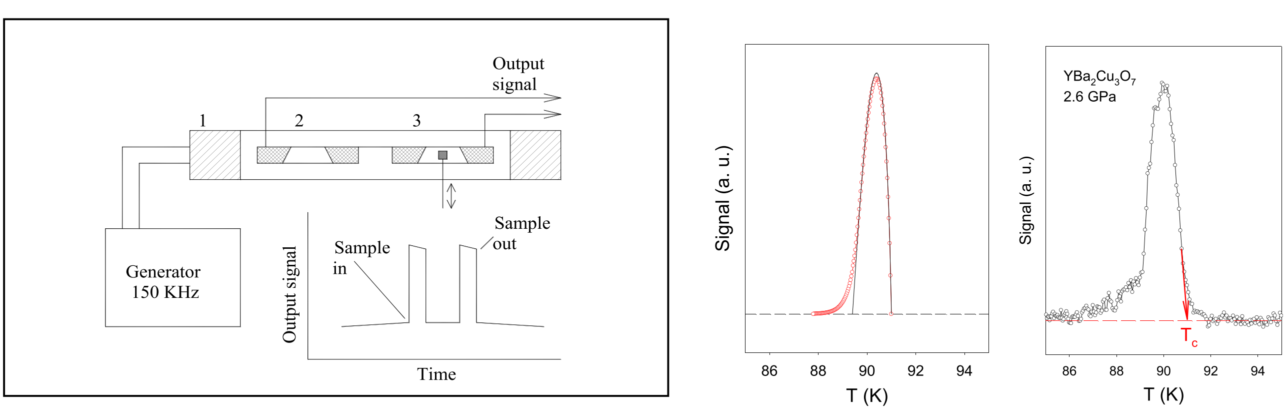

FIG. 7. Left panel: Schematic representation of the background subtraction principle in magnetic susceptibility measurements: 1. primary coil; 2. secondary compensating coil; 3. secondary signal coil. Further experimental details can be found in Ref. 38. "Removal" of the sample from the signal coil by applying an external magnetic field over the critical value produces measurable changes in the total output signal. On the right we show a typical signal of a cuprate superconductor compared with a model calculation for type II superconductors—see Ref. 38 for details of the model calculation.

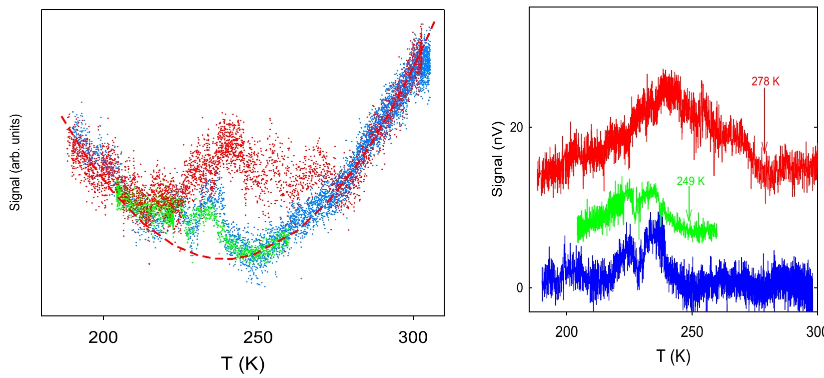

FIG. 8. Left panel shows the magnetic response signals from the LaH_{10} sample in a DAC. The superimposed signals at several pressures are shown by dots: blue—164 GPa, green—169 GPa, red—180 GPa; the background is shown as a red dashed line (approximated by 3rd degree polynomial). Right panel: Signal after background subtraction, shifted in vertical direction (from bottom to top: blue—164 GPa, green—169 GPa, red—180 GPa).

may explain an increase in T_c in the relatively narrow pressure range above the transition. An indirect confirmation can be invoked from the theoretical calculations of T_c in LaH_{10} by Kruglov *et al.*[40]—Fig. 10—who find a dramatic increase in T_c in a narrow pressure range close to 200 GPa from T_c ~ 270 K to nearly 310 K—see Fig. 10. Such an enhancement of T_c was not found in the calculations by Liu *et al.*[22] (Fig. 10), and they did not show any calculated T_c data below 205 GPa. Given the relatively large pressure gradients in the samples, such a transition is easy to miss, especially if the whole volume of the sample is not probed, as in resistivity studies. We note here that only one pressure point in the range 173–203 GPa is reported in the paper by Drozdov *et al.*[26]

In the recent arXiv contribution, Errea *et al.*[31] calculated T_c values for the LaH_{10} Fm-3m phase, taking into account the stabilization of the Fm-3m structure by quantum atomic fluctuations. They found that quantum fluctuations stabilized the Fm-3m phase down to 140 GPa, and found T_c values in agreement with Drozdov *et al.*[26] It is not currently clear why the transition to the R-3m phase, reported by Geballe *et al.*,[24] is not reproduced in this quantum fluctuations approach, but it is evident that such calculations are missing the soft mode scenario we discussed above.

Kruglov *et al.*[40] also presented a T_c calculation for the R-3m phase of LaH_{10} and obtained T_c ~ 200 K at 150 GPa, which is significantly lower than reported T_c's at 150 GPa (~250 K).[26] The reason for this discrepancy is not clear, and further, more extended theoretical efforts would be helpful in understanding how the soft mode may influence T_c in the LaH_{10} samples around the dynamic instability pressure range.

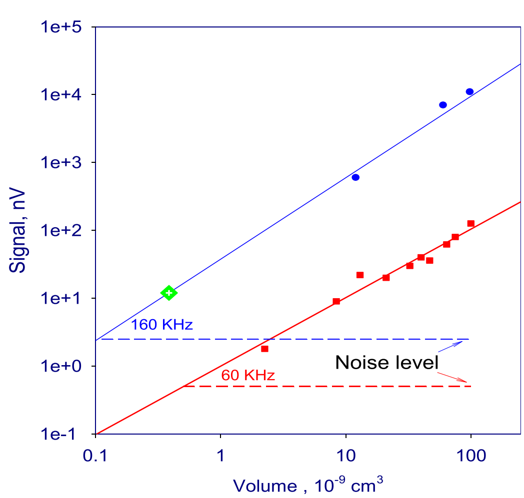

FIG. 9. Calibration curves for two setups operating at two different excitation frequencies.[35] The samples used for calibrating the amplitude of the response are various high-T_c cuprates, Nb, and MgB_2. The practical sensitivity limit for the 160 KHz setup is around $10^{-10} - 2 \times 10^{-10}$ cm^3, which is more than one order of magnitude lower in comparison with the typical sensitivity limit (10^{-8} e.m.u.) of an MPMS system from Quantum Design.

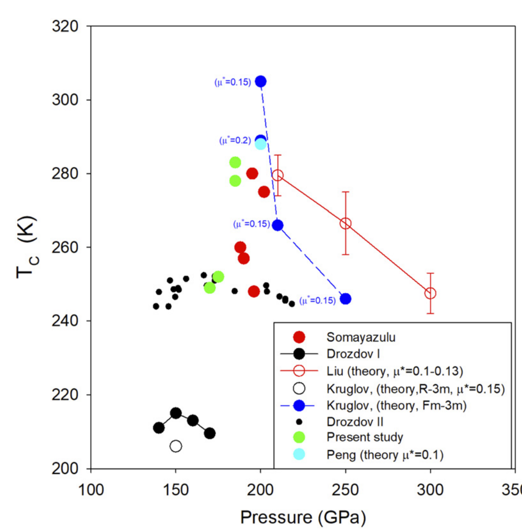

FIG. 10. Summary of the available experimental and theoretical data of superconductivity in LaH_{10}. Sources for the data: Somayazulu *et al.*,[25] Drozdov I *et al.*,[32] Drozdov II *et al.*,[26] Liu *et al.*,[22] Kruglov *et al.*,[40] and Peng *et al.*[21]

IV. NEW SUPERCONDUCTING SUPERHYDRIDES YH_6 AND ThH_{10}

In a recent arXiv publication, Troyan *et al.*[41] reported a superconductivity of up to 224 K in a YH_6 superhydride, which confirmed earlier predictions of a high T_c in this material,[21,42] albeit with lower experimental T_c values. We show structural determination and T_c measurements using a resistivity technique in Figs. 11 and 12, respectively. The x-ray diffraction of the T_c = 224 K sample shows predominantly the YH_6 phase (Fig. 11). Some other minor phases have been observed, including I4/mmm-YH_4 and Imm2-YH_7 at pressures of 160–180 GPa. The synthesized Im$\bar{3}$m-YH_6 shows a clear superconducting transition with a T_c of 224 K at 166 GPa. This value of T_c is lower than most theoretical predictions, which produce T_c's in the range 260–280 K for YH_6.[21,42,43] While being lower than theoretical predictions, this is the third-highest critical temperature that has been experimentally measured in superhydrides. The lower experimental T_c values may be due to strong anharmonicity effects and quantum effects, as recently discussed for LaH_{10}.[31]

Another superconducting hydrides report was released in arXiv in 2019 by Semenok *et al.*[44] claiming ThH_{10} with T_c = 161 K at 174 GPa and ThH_9 with T_c = 146 K at 170 GPa. The superconductivity was measured from the resistivity drop to zero and confirmed by suppression of the transition in the magnetic field. The corresponding experimental results are summarized in Fig. 13. The *fcc*-ThH10 was predicted to have a stabilization pressure of 85 GPa, which makes it unique among known high-T_C metal superhydrides, however, the experimental T_c values were reported only at 174 GPa. In this material, theory predicts a T_c of up to 241 K at 90–100 GPa,[45] and T_c = 160 K at 174 GPa;[44] the latter value is close to the experimental value of 161 K. The predicted T_c for ThH_9 at 150 GPa is 123–145 K, which is not far from the experimental value of 146 K at 170 GPa.[44] Overall, it appears that the predicted and measured T_c values in thorium superhydrides are very similar, contrary to what is found in LaH_{10} and YH_6 materials, where anharmonic or quantum effects may play a significant role in defining the T_c values in the materials.

Notes added in review: After this paper was submitted for review, an important arXiv contribution was published on experimental studies of superconductivity in the new YH_6 and YH_9 phases.[46] T_c = 227 K was observed for a YH_6 sample at 237 GPa, and a T_c of YH_9 had a dome-like shape as a function of pressure with a maximum T_c = 243 K at 201 GPa. Notably, the observed T_c's are lower by ~30 K than the predicted T_c's, similar to our observation for the YH_6 sample. We refer the reader to the original publication for further details.

V. PERSPECTIVES FOR FUTURE ROOM-TEMPERATURE SUPERCONDUCTIVITY STUDIES

With the available experimental data on superconducting superhydrides, we may summarize a few empirical facts related to their structural and superconducting properties. In Fig. 14, we show the highest T_c values predicted by theory in superhydrides,[47] which are similar to the highest T_c values observed in pure elements under high-pressure conditions (available at http://www.hpr.stec.es.osaka-u.ac.jp/e-super). Both periodic table representations look strikingly similar. Indeed, from previous theoretical predictions we know that metal superhydrides with clathrate-like hydrogen lattices at the beginning of the period (but not pure alkali metal hydrides) are predicted to have high T_c values.[21,48] Similarly, most of the elements at the beginning of the period (Ca, Y, Sc) show quite high T_c values at high pressures. This correlation does not look coincidental if we adopt the "doped" hydrogen approach. Metal ions are embedded in the hydrogen "clathrate" lattice, and when the surrounding electronic density is optimized so that the pure metal exhibits high T_c values, the "encaged" metals may contribute substantially to electron-phonon coupling in the material. It is possible that such an approach may give better superconducting materials if ternary compounds are used, allowing continuous tuning of the electronic density. Indeed, for ternary compounds very high T_c values are predicted for a few materials, such as Li_2MgH_{16}[23] with a predicted T_c ~ 473 K at 250 GPa.

Another important observation is the systematic trends in the partial volume occupied by the hydrogen atom in high-T_c superhydrides. For example, in Fig. 15 we show a comparison of hydrogen partial volume in various hydrides, including high-T_c phases. It is evident that the partial volume for the hydrogen atom in proven

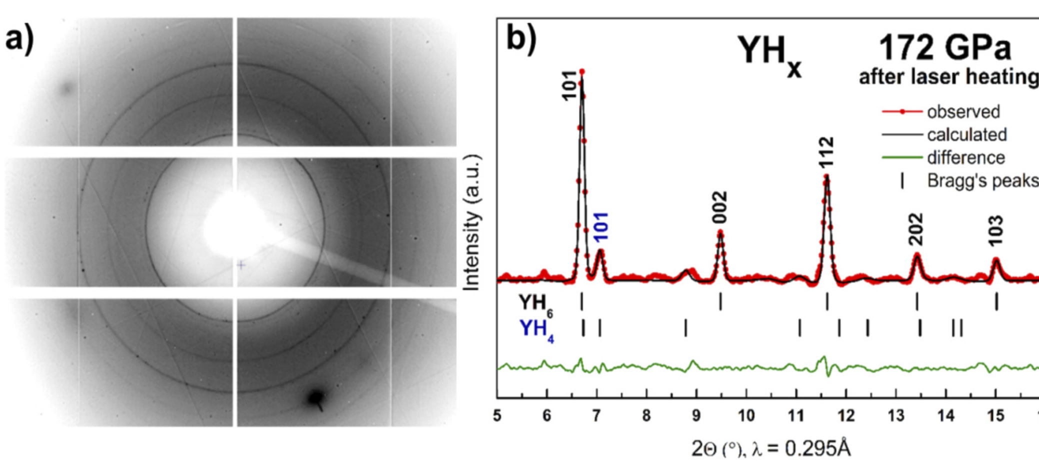

FIG. 11. Troyan *et al.*[41] (a) XRD pattern of M3 sample at 172 GPa recorded at λ = 0.2952 Å; (b) Le Bail refinements for Im$\bar{3}$*m*-YH6 and *I4/mmm*-YH4. Red circles are experimental data; black line is the fit; green line shows residues.

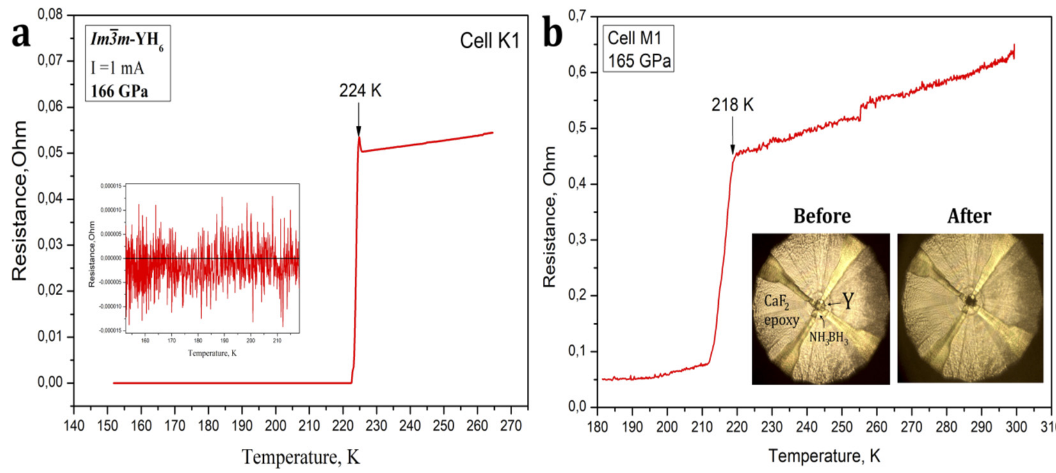

FIG. 12. Troyan *et al.*[41] Superconducting transitions in Im$\bar{3}$*m*-YH6: (a) Dependence of electrical resistance on temperature. Inset: the resistance drops to zero after cooling below T*C*; (b) jump in *R*(*T*) dependence of resistance (nine times increase) on temperature for the second sample.

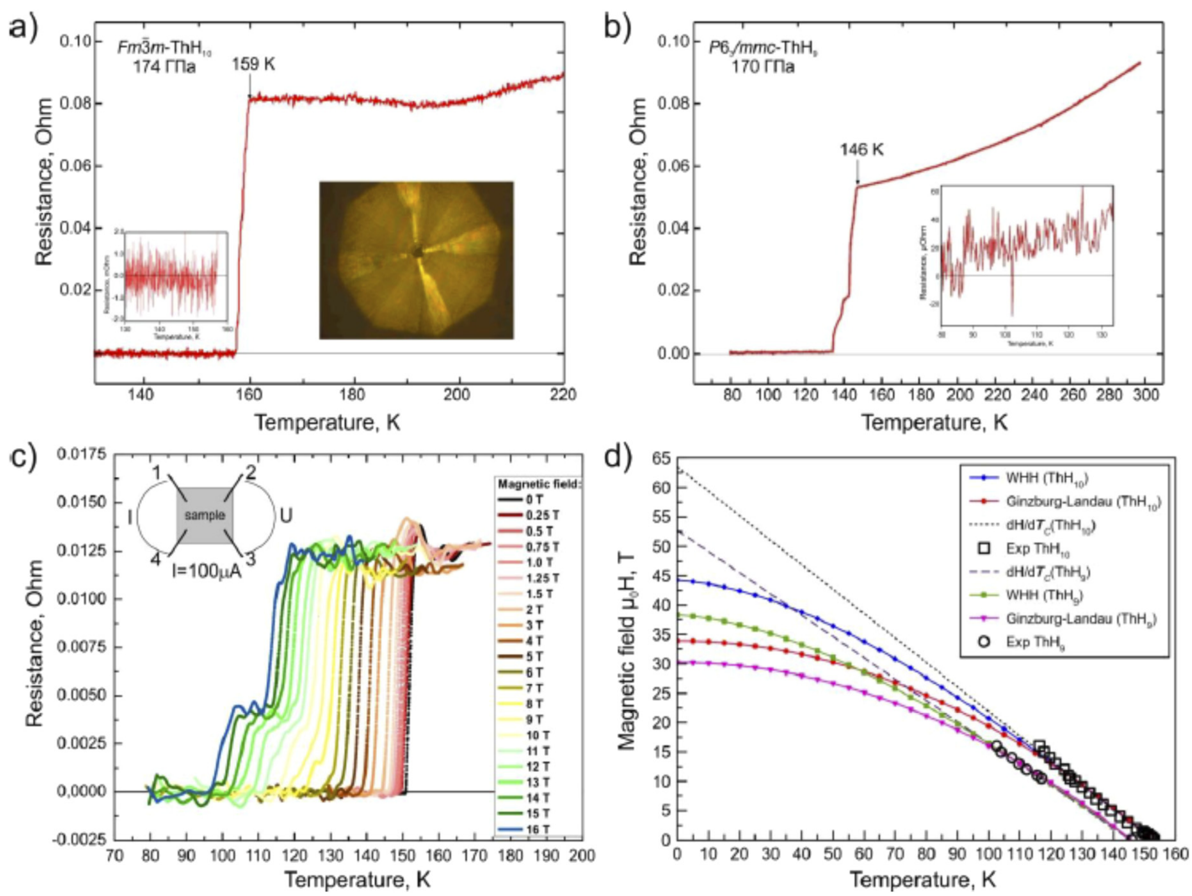

FIG. 13. Semenok *et al.*[44] Observation of superconductivity in (a) ThH_{10} and (b) ThH_9. The temperature dependence of the resistance (R) of thorium superhydride was determined in a sample synthesized from Th+NH_3BH_3. The resistance was measured using four electrodes deposited on a diamond anvil with the sample placed on top of the electrodes [Fig. 15(a), inset] with an excitation current of 100 μA. The resistance near the zero point is shown on a smaller scale in the insets; (c) dependence of the resistance on temperature under an external magnetic field at 170 GPa; (d) dependence of the critical temperature (T_c) of ThH_{10} and ThH_9 on the magnetic field.

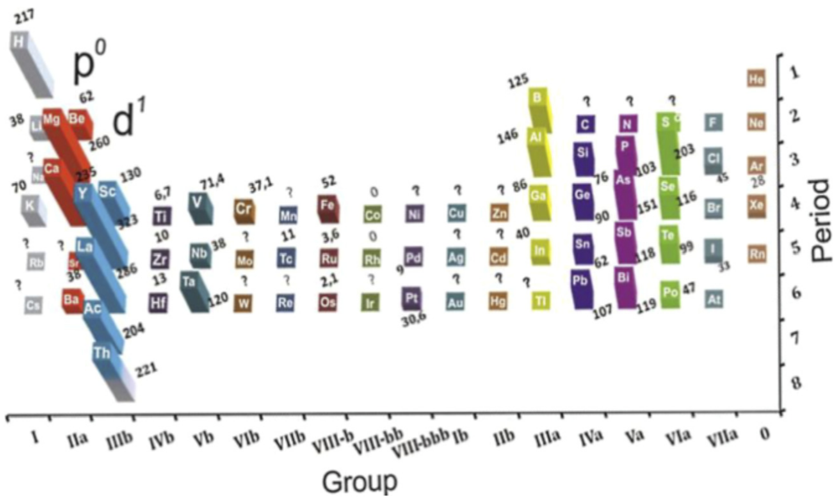

FIG. 14. High-T_c superconducting superhydrides,[47] which is very similar to the highest T_c in elements under high pressure conditions (see e.g., http://www.hpr.stec.es.osaka-u.ac.jp/e-super) [The figure is reprinted with permission from supplementary material in Semenok *et al.*, J. Phys. Chem. Lett. **9**(8), 1920–1926 (2018). Copyright 2018 American Chemical Society.].

high-T_c superhydrides is above the value calculated for hypothetical atomic metallic hydrogen[49] and is much lower in several nonsuperconducting hydrides like AlH_3, FeH_3, FeH_5. This may be related to the augmented electron density around the hydrogen atom in superconducting superhydrides. It is interesting that the atomic hydrogen volume in high-T_c materials, like LaH_{10} and ThH_{10}, is very close to the partial volume of hydrogen in compressed solid H_2. Overall, the equation of state for metallic atomic hydrogen serves as a dividing line between superconducting and nonsuperconducting hydrides in Fig. 15. In the context of "doped" metallic hydrogen, as suggested by Ashcroft,[15] it appears that the hydrogen clathrate sublattice in superhydrides is "overdoped" in comparison with the atomic metallic phase of pure hydrogen.

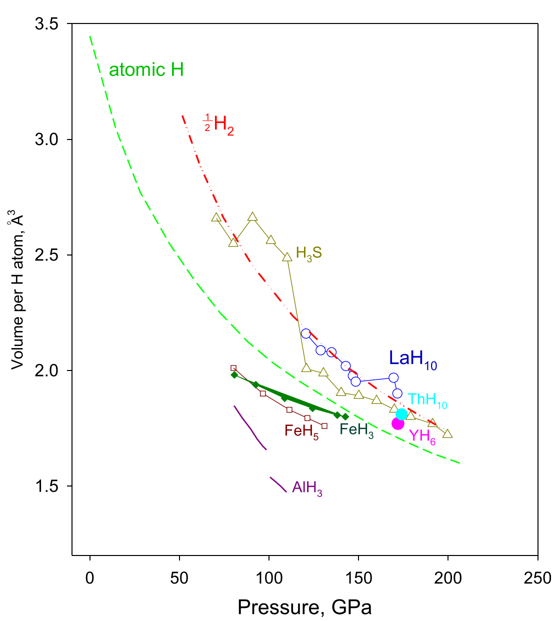

FIG. 15. Comparison of atomic volumes per hydrogen atom in high-T_c and nonsuperconducting hydrides. The equation of state for hypothetical atomic hydrogen (green dashed line) is taken from Pepin *et al.*,[49] as well as atomic H volumes for FeH_3 and FeH_5. The H_2 volume is from Loubeyre *et al.*[50] LaH_{10} and AlH_3 data are taken from Geballe *et al.*[24] ThH_{10} is taken from Semenok *et al.*,[44] YH_6 from Troyan *et al.*[41] H_3S data are given as calculated in Ref. 51.

We believe that the volume differences given in Fig. 15 are quite robust, since we have a very good match between the theoretical and experimental volumes of superhydride phases, for example in thorium[44] and yttrium[41] superhydrides. In that respect, the partial hydrogen volume may become a very sensitive probe of the "doping" state of hydrogen in superconducting hydrides. It would be interesting to explore the optimum doping condition for clathrate hydrogen lattices, which can be done by studying ternary compounds.[23]

The clathrate hydrogen cages in superhydrides are stable only above 100–150 GPa in most studied materials. In that respect, ThH_{10} stands out as a predicted viable candidate for high-T_c superconductivity below 100 GPa.[44] It would be interesting to check these predictions experimentally. It is not clear what makes thorium hydrides more stable at lower pressures, but experimentalists may certainly benefit from such predictions of lower pressure, high-T_c hydrides.

VI. CONCLUSION

In this brief review we summarized what is known about new superconducting hydrides (superhydrides) that have exceptionally high critical superconducting temperatures. We provided the latest magnetic susceptibility data for LaH_{10}, showing the possibility of high-T_c phases with T_c's of up to 280 K. The mechanism for the enhancement of T_c in LaH_{10} was also suggested, based on a soft mode scenario in the vicinity of the Fm-3m to R-3m phase transition in LaH_{10}.[24]

We introduced new experimental data on YH_6 and ThH_{10} in the context of "doped" metallic hydrogen. It appears that the partial hydrogen volume in such superhydrides may be a good indicator of "doping." In superhydrides, based on partial volume arguments, we suggest that the hydrogen sublattice may be "overdoped" with respect to (hypothetical) pure metallic hydrogen. Overall, the concept of doping may prove very useful in studying ternary superhydrides and is an excellent tool in tuning the doping levels of the hydrogen sublattice.

While at the moment it appears that superconducting superhydrides lack practical importance due to their stability range in the hundreds of GPa, the scientific challenge of the field is enormous and promises exciting times. Room-temperature superconductivity has almost been achieved experimentally, and increasing numbers of theoretical predictions show significantly high T_c's, even well above the boiling point of water.[23] The experimental challenge is much harder than the theoretical one, but we believe most theoretical predictions will be tested in the near future.

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