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Discussion

Public debate on metallic hydrogen to boost high pressure research

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Abstract

Instead of praises from colleagues, the claim of observation of metallic hydrogen at 495 GPa by Dias and Silvera met much skepticism, and grew into a public debate at the International Conference on High-Pressure Science and Technology, AIRAPT26. We briefly review this debate, and extend the topic to show that this disputation could be an opportunity to benefit the whole high pressure community.

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It is well known that public debate has been playing a pivotal role in the history of science. One of the well-known cases is the Bohr-Einstein debate, which greatly boosted the development of quantum mechanics. Recently, a similar debate appeared at *the International Conference on High-Pressure Science and Technology*, AIRAPT26, an important gathering of global high-pressure experts, on a recent claim of metallic hydrogen.

Metallic hydrogen (MH), referred to hydrogen in a metallic state [1], is dubbed as the *Holy Grail* in the high-pressure community. Quantum mechanics tells that every material can come into metallic state under high enough compression, which should also be the case for hydrogen. However, things became fascinating when Ashcroft added a flavor into it by predicting that MH could become superconducting at room temperature [2], as well as accompanying bizarre and interesting phenomena might be observed when protons became quantized [3,4]. These predictions together with the possibility that MH could be a strong explosive with ultra-high energy density, make MH a wonder material attracting the attention of experimentalists in high-pressure community. However, the challenge in pursuing MH is tremendous due to the notorious activity of hydrogen. Modern accurate theories predict that the transition into MH happens at a pressure ~500 GPa [5,6], whereas the most advanced diamond anvil cell (DAC) used for compression is limited to ~400 GPa on hydrogen. It is a huge surprise to the high-pressure community when Dias and Silvera (DS) claimed that they have achieved a pressure as high as 495 GPa and obtained MH in laboratory [7]. Their statement immediately caused backfire, and at least four leading groups in this field doubted the authenticity of the sensational discovery [8–12]. This fierce debate eventually went to public at the AIRAPT26 conference, held in Beijing in August 2017.

The debate mainly focused on three points: (1) the pressure calibration problem, (2) the credibility of the diamond Raman spectrum which implied a pressure of 495 GPa, and (3) whether the observation of reflectance alone is sufficient to claim the generation of MH. Without any internal pressure calibration, DS relied on a very special secondary pressure scale, the linear extrapolation of the load curve, to guide the DAC loading in the blind stage (>335 GPa) [7]. In principle, this is valid if the pressure of the final state could be reliably

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determined. But the possible interference from fictitious Raman peaks, which are frequently encountered at high pressures before the diamonds break, as Eremets pointed out [10], suggests that only one Raman spectrum is not enough to completely pin down the final pressure reliably. People thus have to resort to the peculiar linear load curve to establish their judgment, which unfortunately has not been widely tested and accepted [8−11]. That is the reason why Loubeyre [11] and others wanted to see the continuity variation in the pressure scale and the pressure distribution across the chamber before accepting the claimed pressure record. Scarce data is always concomitant with unknown uncertainty, and is less convincing.

Fortunately, at AIRAPT26, an important proposal was announced to establish an international pressure standard to solve this problem. In the near future, this kind of dispute on pressure calibration could be greatly reduced by bringing all different works into one pressure standard. This, of course, takes some time. A realistic option currently available to resolve the dispute is to reproduce more reliable data on DS side. Reproducibility is the only option against suspicion. It is challenging but doable for DS, considering their reported high possibility to reach a pressure >400 GPa on hydrogen [9]. The reported Raman spectrum of diamond in Ref. [7] should be repeated first [10], as long as a pressure of 495 GPa is reached, no matter on hydrogen or on other inert materials. This spectrum can be verified or disproved by DS or other groups. The concern about the load curve can also be eliminated by sharing their unique DAC device with the community or inviting a third party to participate in their experiments.

The basis for DS to claim the discovery of MH is the observed high reflectance. No one doubts that they have observed the metal-like reflectance. The key problem is that what actually caused the high reflectivity. Eremets [10] and Loubeyre [11] have proposed their respective interpretations. Eremets also raised concerns about the pressure measurements and noted that he has observed a reflection and semi-metallic behavior of hydrogen at a lower pressure of 360 GPa and 100 K [17,18], which is beyond his understanding that DS only found a reflection at 500 GPa and 80 K. Nonetheless, DS insisted that the reflection must come from MH by adopting a Drude model analysis [7,12]. However, fitting of the reflectance data to a Drude model could be problematic, since (i) MH at ~500 GPa does not behave like a free-electron metal at low energy regime and cannot fit into a Drude model [13], and (ii) as Borinaga et al. pointed out, there is a large space of ambiguity in this nonlinear fitting with just two data points [13]. The fact that the two low-energy reflectance points match well with a recent independent theoretical analysis [13], and another two points at a higher energy, though without any correction for the diamond absorption, qualitatively follow the predicted depression due to a unique interband plasmon at 6.2 eV in MH, is an encouraging message for DS. But a careful and reliable diamond absorption correction [8] must be made before one can tell whether it really corresponds to the MH fingerprint in reflectivity or not. In addition, hydrogen experiments often end with the formation of incipient cracks in diamond anvils that lead to the loss of hydrogen sample, and the Drude-like reflectance spectra could actually come from the metallic gasket filling the empty sample chamber. In particular, the IR spectra measured by Loubeyre et al. show different data from those reported by Silvera et al. in the pressure range of overlap [11], which further undermines the credibility of Ref. [7]. To demonstrate the presence of hydrogen sample and that the reflectance indeed comes from hydrogen, DS need to show the diagnostic hydrogen Raman peaks during the releasing pressure.

A clear message from this public debate is that we are now very near the discovery of MH. DS might have taken a leading position in this experimental race. But it might be too early for DS to make the final claim [8−11]. They must present a reliable pressure calibration, demonstrate the retainment of hydrogen sample, and reproduce the results before any solid conclusion can be reached. Substantial measurements other than the reflectance are also required.

One important aspect was ignored or downplayed in this debate—the metastability and recovery of MH at ambient conditions. Nellis raised the importance of this topic without concrete responses. In Ref. [7], DS referred to Ref. [14] for the justification of recoverability of MH. This could be wildly optimistic. Actually, an exploration of the possible energy barriers in MH at ambient pressure with accurate modern density functional theory (DFT) and NEB method unfortunately revealed that MH could be highly unstable at ambient pressure [15]. We extend a similar analysis at relatively high pressures here to investigate that at what pressure can MH be metastable. Both the degenerate Cs-IV and Fddd phases have been studied. We only focus on Fddd phase below as the conclusion is the same for Cs-IV.

At first, we explored the superheating limit of MH down to 200 GPa, using AIMD in PBE approximation of DFT as implemented in VASP. With a large cell containing 480H, a *k*-point grid of 2 × 2 × 2, and an energy cutoff of 600 eV, we found that the classical superheating temperature of MH within this pressure range is very low, as shown in Fig. 1(a). If taking into account the nuclear quantum effects of protons, the superheating limit should lower further. The indication is that one cannot have MH, even in a metastable state, at a pressure less than 200 GPa and a temperature as low as 100 K. This conclusion is further strengthened by a NEB energy barrier calculation using both PBE and vdW-DF functionals. It is well known that DFT has some problems in describing the H_2 dissociation. But both accurate QMC calculations and dynamic compression experiment showed that the true physics in dense hydrogen around dissociation should be well bracketed by PBE and vdW-DF functionals [16]. We thus employed both methods to avoid possible bias. The results for 315 GPa is given in Fig. 1(b). A very weak barrier (in both PBE and vdW-DF) of about 0.03 eV/H is observed. This value corresponds to a temperature of 348 K, being consistent with the superheating temperature. This barrier reduces rapidly with further decreasing pressure. The conclusion is that MH cannot be recovered to low pressure with traditional methods.

As mentioned above, the importance of MH lies not in the metallization itself, but mainly in the potential application of

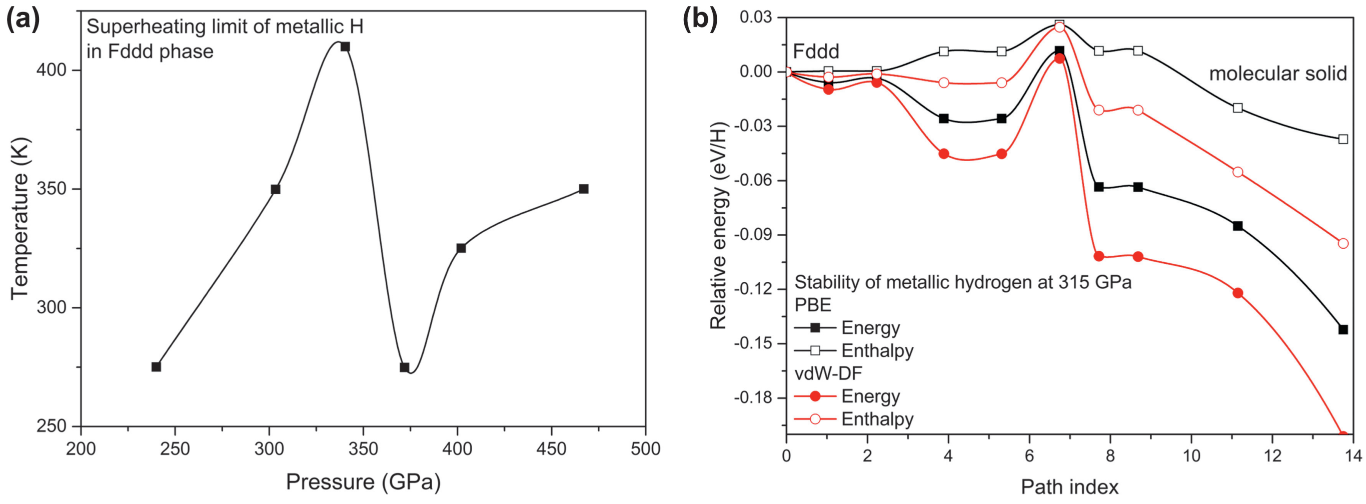

Fig. 1. (a) Classical superheating limit and (b) energy barrier calculated for MH in Fddd phase using AIMD and NEB methods at the DFT level.

MH as a test model for quantum many-body theory at very high density, and as a room temperature superconductor or a high energy density material, as well as the capability to turn this wonder material into real product. MH might have a huge and deep impact on the future of mankind. There is no precedent in high pressure community with such a possible direct entanglement in civilization development. To obtain MH at high pressure condition is challenging enough, and to retrieve it back to ambient conditions is even much more challenging, requiring unconventional and extraordinary creativity. It is hard to say of having grabbed the *Holy Grail* by just observing it. The public debate on MH, fortunately, could greatly boost high pressure research as the top experimentalists are unveiling their secret weapons and special techniques, as well as sharing their unique experience of achieving such high pressures on such a difficult material. This still ongoing public debate undoubtedly will attract and gather talent young scientists continuously into this promising field, to foster and create novel techniques that will eventually pave the way towards a bright future.

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