Dense quantum hydrogen

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Ultracondensed fluid metallic hydrogen has been made at high pressures. Solid metallic H would have several scientific and technological applications if metallic fluid hydrogen made at high pressures could be quenched metastably to a solid at ambient. The quantum nature of dense hydrogen is an issue both at high pressures and in materials recovered metastably on release of pressure. Quantum zero point vibrations of H might have a significant affect on properties of metallic H at high pressures and might adversely affect lifetimes of metastable solid hydrogen, which is particularly relevant for applications. Metallic (degenerate) fluid H has been made at finite temperatures with a reverberating shock wave under dynamic compressions and under static compressions in laser-heated diamond-anvil cells. The pressure-temperature (P–T) regime in those experiments ranged up to 180 GPa and 3000 K, in which metallic fluid H is a quantum-degenerate fluid with $T/T_F << 1$, where T_F is Fermi temperature. The lifetime of an experiment under static compression near 500 GPa at 5.5 K ranged up to weeks, sufficiently long to warrant concern about quantum diffusion having a major affect on the chemical composition of that metallic sample.

Keywords: ultracondensed metallic fluid, metallic hydrogen, high pressure.

1. Introduction

Ultracondensed metallic fluid H has been made at high pressures by several groups. Solid metallic H would have several scientific and technological applications if metallic hydrogen made at high pressures could be quenched metastably to a solid at ambient pressure. Toward that end, experimental results and theoretical calculations about metastability in general have been reviewed [1].

The quantum nature of dense hydrogenous materials is an issue at high pressures and in materials recovered metastably on release of high pressure. Quantum zero point vibrations of H, for example, might adversely affect lifetimes of metastable hydrogenous solids, which is particularly relevant for technological applications. The purpose of this paper is to assess the quantum nature of reported cases of dense metallic H.

At density $\rho_m = 0.62$ mol H/cm^3, "very low temperatures" and some pressure P greater than 25 GPa ($0.25 \cdot 10^6$ bar = = 0.25 Mbar), Wigner and Huntington predicted that electrically-insulating diatomic H_2 would undergo an insulator–metal transition (IMT) via molecular dissociation to monatomic H [2]. Density ρ_m is 9-fold the density of H in liquid H_2 at 20 K. At that density the free-electron Fermi temperature of metallic H is $T_F = 220,000$ K. Low finite temperatures of a metal are those of a quantum-degenerate electron system

[3]. Thus, dense metallic H is expected to be quantum in nature ($T/T_F << 1$) for T of order a few 1000 K or less.

Dynamic compression [4] and static compression have been used to achieve metallic H at high P. Dynamic compressions have been generated by hypervelocity impact of metal plates accelerated with a two-stage light-gas gun to velocities as high as 8 km/s, with chemical explosives and by intense optical irradiation from a pulsed laser. Lifetimes of those dynamic experiments range between a few 100 ns down to a few 10 ns.

Time at high pressures is an important consideration. Dimensions of cylindrical specimens in dynamic experiments are generally such that $D/d \approx 20$, where D is diameter and d is thickness. This shape and size maintain the central volume of a specimen free from effects of pressure release at sound speed from their edges. Lifetimes of dynamic compressions are sufficiently long to achieve thermal equilibrium at high P in dense hydrogen and too brief for undesirable effects to occur, such as thermal and mass diffusion of H out of specimen volume during experimental lifetime.

Lifetimes of static compressions in a diamond-anvil cell (DAC) ranged from hours to days in laser-heated DACs. An experimental lifetime in a DAC near 500 GPa at 5.5 K ranged up to weeks, sufficiently long to warrant concern about the occurrence of unexpected negative effects on the

specimen at late times. Historically, lifetimes of static compressions are not constrained. Perhaps in some cases, particularly for hydrogenous samples, experimental lifetimes of static experiments would best be reported for reasons discussed below.

2. Experimental results

Metallic fluid H (MFH) has been made under quasi-isentropic dynamic compression at pressures P and temperatures T achieved with reverberating shock waves [5–9]. Extreme thermodynamic states were achieved mechanically by conservation of mass, momentum and energy on each reflection of supersonic matter waves in H reflected off solid anvils. Electrical conductivities of dense fluid H were measured with metal probes inserted through an Al_2O_3 anvil with measured negligible electrical conductivity. Liquid-H_2 specimens were initially 20 mm in diameter and 0.5 mm thick [5,6]. The crossover from semi-conductivity to poor metal [5,6] with Mott's minimum metallic conductivity (2000 (Ohm·cm)$^{-1}$) [10] occurred in experiments with 100 ns lifetimes. Reverberation completed at $P = 140$ GPa, $T \approx 3000$ K, $T/T_F = 0.014$ at density ρ_m predicted by Wigner and Huntington (WH) [2]. Those P/T are above the critical point P_c/T_c of the dissociative phase transition. Thus, that crossover is continuous from H_2 to H with increasing P/T. Similar results were measured in [7].

Using shock reverberation, electrical resistivities of fluid silane (SiH_4) have been measured up to 106 GPa [8]. Although the metallization transition at 140 GPa could not be confirmed because of the impact velocity limit and thus shock-pressure limit (106 GPa) of their two-stage light-gas gun, measured electrical resistivity of fluid silane drops sharply with increasing pressure as reported previously for fluid hydrogen [5–7]. This virtual coincidence in the semiconducting regime is attributed to decomposition of SiH_4 into Si + 4 H with fluid H providing the major contribution to electrical conductivity.

Quasi-isentropic compression of liquid D_2 has been achieved with shock reverberation generated at the National Ignition Facility (NIF) to increase P substantially slower than does a singe sharp shock-wave front. In a series of such experiments at temperatures below 2000 K, a transition to metal-like reflectivity above 30% was observed in fluid D near 200 GPa [9]. Metallization results in [9] and [5,6] are in good agreement, given the different compressive and diagnostic techniques employed.

Metallic states of hydrogen have also been made under static compression in laser-heated DACs at high P and finite T selectively along the dissociative phase transition curve [11,12]. The diagnostic in those experiments was energy of optical radiation incident on compressed H and the relative amounts of optical reflection, absorption and transmission. Pressures and temperatures achieved in the fluid under dynamic (93–180 GPa/1700–3100 K) and static

(82–170 GPa/1100–2500 K) compressions are comparable, although the trajectories in P–T space achieved under static and dynamic compression differ because they were achieved by different methods [4].

The above metallic fluids were made by both dynamic and static compressions. Temperatures ranged between 1100 and 3000 K and pressures ranged between 82 and 140 GPa. At these high temperatures and associated high densities metallic fluid H and D are quantum mechanically degenerate ($T/T_F << 1$). In this P–T regime, these metallic fluids act as traditional metallic liquids.

3. DAC experiment at 5.5 K near 495 GPa

A single observation of metallic H has been reported under static compression in a DAC at 5.5 K at an estimated pressure of 495 GPa [13]. Optical reflectivity characteristic of a metal was observed visually and measured in reflected light. Obtaining such a high pressure in such a compressible sample in a DAC is a major accomplishment and an interesting scientific result. However, although metallic reflectivity was observed, there is a question as to the chemical composition of the reflecting surface. The low temperature of 5.5 K in 15-fold compressed H means that quantum zero-point vibrations of dense H need to be considered in the analysis.

To prevent breaking diamonds in the DAC the compression to 500 GPa was done slowly, on the time scale of weeks, which process was successful. The key portion of the sample consisted of a ~1 μm-thick layer of hydrogen followed by an initially 50 nm-thick layer of alumina (amorphous Al–O) deposited on the diamond flats of the DAC. The alumina layer was assumed to be a "diffusion barrier" of H into the diamond anvil. Reflectivity was assumed to be from metallic H through the alumina, which was assumed to be transparent at 500 GPa. Assuming transparency of pure alumina is reasonable because the calculated Hugoniot at high temperatures of Al_2O_3 does not become metallic until 900 GPa [14]. Conventional non-quantum diffusivity is a thermally-activated process. In [13] H diffusion into alumina was assumed to be zero because of the low temperature of 5.5 K and the assumption that H diffusion into alumina is thermally-activated.

However, dense H has intrinsic quantum zero-point vibrations (ZPV) at 5.5 K, which are not thermally activated. ZPV represent jump attempts of H to diffuse into alumina. Because of the high density of alumina at 500 GPa, the diffusivity coefficient of H into alumina is expected to be smaller than at ambient, whatever that value is, but nevertheless finite (non-zero) at high P. The weeks-long duration of that experiment imply the possibility that after some of that time a significant quantity of H might have diffused into the alumina. Thus, even with a small diffusivity coefficient of H into and through alumina, after a sufficiently long time it is possible that an amorphous Al–O–H alloy formed and might

have become metallic with high reflectivity at 500 GPa, as would many insulators at such a high pressure.

Thus, there are at least two possible explanations with different reflecting surfaces as the source for the observed reflecting metallic surface [13]. In one case, no H diffused into alumina, which remained nonmetallic and transparent up to ~500 GPa, near which pure H underwent a transition to metallic H. In the other case, quantum ZPV generated a sufficient number of H atoms that diffused through the 50 nm thick alumina to form an amorphous Al–O–H alloy near 500 GPa, which became metallic with high reflectivity, as would many insulators near 500 GPa. At present the only thing known in this newly accessed regime of ultrahigh *P* and cryogenic *T* is that a reflecting surface was formed near 500 GPa with a chemical composition that needs to be determined.

At this point at least two experiments in a DAC at 5 K are appropriate: (i) find a spectroscopic non-contact technique to determine the chemical composition of the reflecting surface near 500 GPa and (ii) measure the diffusion constant of H atoms through various thicknesses of say 10–50 nm of alumina at 500 GPa. Results in [13] indicate that at extremely high densities and low temperatures it is possible to measure properties of materials whose composition is unknown because of ZPV quantum effects in hydrogen. For this reason documentation of the measured pressure, etc. histories and diagnostic characterizations are useful for potential attempts to reproduce such observations.

4. Dense quantum matter

The above analysis suggests that perhaps the most scientifically interesting aspect implied by consideration of 15-fold compressed H at 5 K is the general issue of the nature of dense quantum protium — the isotopes of hydrogen (H, D and T), which would include the question of metallization of H. Study of protium offers the prospect of checking mass-scaling relationships for quantum phenolmena in the lightest element. Interesting discoveries for H and D might motivate research on T with its additional issues of handling a radioactive material.

Such protium studies would involve both theory and experiment. Important issues include (in no particular order): (i) finding high-pressure protium phases, for example as in [15], (ii) finding zero-point energies of dense protium, (iii) learning how to quench novel hydrogenous (and protium) phases made at high pressures to metastable solids at ambient using methods implicit in [15], (iv) determining whether the ground states of dense hydrogen (and protium) is solid or fluid [16], and of course (v) determining quantitatively thicknesses of diffusion barriers at 5 K calibrated versus pressure for H (and protium). The latter point is a potential way to study the nature of quantum zero-point vibrations themselves.

1. W.J. Nellis, *J. Phys.: Condens. Matter* **29**, 504001 (2017).
2. E. Wigner and H.B. Huntington, *J. Chem. Phys.* **3**, 764 (1935).
3. N.F. Mott, *The Theory of the Properties of Metals and Alloys*, Dover Press, New York (1936).
4. W.J. Nellis, *Ultracondensed Matter by Dynamic Compression*, Cambridge University Press, Cambridge (2017).
5. S.T. Weir, A.C. Mitchell, and W.J. Nellis, *Phys. Rev. Lett.* **76**, 1860 (1996).
6. W.J. Nellis, S.T. Weir, and A.C. Mitchell, *Phys. Rev. B* **59**, 3434 (1999).
7. V.E. Fortov, V.A. Ternovoi, M.V. Zhernokletov, M.A. Mochalov, A.L. Mikhailov, A.S. Filimonov, A.A. Pyalling, V.B. Mintsev, V.K. Gryaznov, and I.L. Iosilevskii, *J. Exp. Theor. Phys.* **97**, 259 (2003).
8. X.F. Zhong, F.S. Liu, L.C. Cai, F. Xi, M.J. Zhang, Q.J. Liu, Y.P. Wang, and B.B. Hao, *Chin. Phys. Lett.* **31**, 126201 (2014).
9. P.M. Celliers, M. Millot, S. Brygoo, R.S. McWilliams, D.E. Fratanduono, J.R. Rygg. A.F. Goncharov, P. Loubeyre, J.H. Eggert, J.L. Peterson, N.B. Meezan, S. Le Pape, G.W. Collins, R. Jeanloz, and R.J. Hemley, *Science* **361**, 677 (2018).
10. N.F. Mott, *Philos. Mag.* **26**, 1015 (1972).
11. K. Ohta, K.M. Ichimaru, M. Einaga, S. Kawaguchi, K. Shimizu, T. Matsuoka, N. Hirao, and Y. Ohishi, *Nature Sci. Rep.* **5**, 16560 (2015).
12. M. Zaghoo, A. Salamat, and I.F. Silvera, *Phys. Rev. B* **93**, 155128 (2016).
13. R. Dias and I.F. Silvera, *Science* **355**, 715 (2017).
14. H. Liu, J.S. Tse, and W.J. Nellis, *Nature Sci. Rep.* **5**, 12823 (2015).
15. D. Plasienka, R. Martonak, and E. Tosatti, *Nature Sci. Rep.* **6**, 37694 (2016).
16. V. Labet, R. Hoffmann, and N.W. Ashcroft, *J. Chem. Phys.* **136**, 074504 (2012).

Щільний квантовий водень

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Ультраконденсований рідкий металевий водень отримано при високому тиску. Металевий водень мав би багато наукових та технологічних застосувань, якби міг залишатися в метастабільному стані при нормальних умовах. Питання про квантову природу щільного водню актуальне як при високому тиску, так і для матеріалів, які залишаються метастабільними при скиданні тиску. Квантові нульові коливання можуть істотно впливати на властивості металевого Н при високому тиску і можуть несприятливо позначатися на часи життя метастабільного твердого водню, що особливо актуально для практичних застосувань. Металева (вироджена) рідина Н була отримана при динамічному та статичному стисненні в умовах зворотної ударної хвилі в алмазній ковадлі, що нагрівається лазером.

Тиск та температура в цих експериментах становили до 180 ГПа та 3000 К, при яких металева рідина Н являє собою квантово-вироджену рідину з $T/T_F \ll 1$, де T_F — температура Фермі. Час проведення експерименту при статичному стисненні близько 500 ГПа й температурі 5,5 К становив до декількох тижнів, що достатньо для спостереження квантової дифузії, яка має істотний вплив на хімічний склад цього металевого зразка.

Плотный квантовый водород

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Ультраконденсированный жидкий металлический водород получен при высоких давлениях. Металлический водород имел бы много научных и технологических применений, если бы мог оставаться в метастабильном состоянии при нормальных условиях. Вопрос о квантовой природе плотного водорода актуален как при высоких давлениях, так и для материалов, которые остаются метастабильными при сбросе давления. Квантовые нулевые колебания могут существенно влиять на свойства металлического Н при высоких давлениях и могут неблагоприятно сказываться на временах жизни метастабильного твердого водорода, что особенно актуально для практических применений. Металлическая (вырожденная) жидкость Н получена при динамическом и статическом сжатиях в условиях возвратной ударной волны в нагреваемой лазером алмазной наковальне. Давление и температура в этих экспериментах составляли до 180 ГПа и 3000 К, при которых металлическая жидкость Н представляет собой квантово-вырожденную жидкость с $T/T_F \ll 1$, где T_F — температура Ферми. Время проведения эксперимента при статическом сжатии около 500 ГПа и температуре 5,5 К составляло до нескольких недель, что достаточно для наблюдения квантовой диффузии, имеющей существенное влияние на химический состав этого металлического образца.