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Bridgman's high-pressure atomic destructibility and its growing legacy of ordered states

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Abstract

In 1927 P W Bridgman proposed that the otherwise stable structure of atoms could be broken down in the condensed state of matter by mutual encroachment of neighbouring atoms, this being brought about by pressure. Bridgman's principle of destructibility on systematic densification applies equally to molecular systems and from the modern perspective the aftermath of Bridgman's insight is to be sought in structural transitions, in the ensuing but intertwined re-arrangement of electronic states, and generally in the appearance of quite new states of order, both classical and quantal. This pathway is developed in a brief retrospective with examples drawn from hydrogen and light elements, as well as specific hydrogen-rich systems which, as with hydrogen itself, may also offer the prospect of high-temperature superconductivity.

1. Introduction

The pathways that might lead one to a particular field of research and investigation must surely be legion. In my case a turn towards condensed matter at high pressures happened during a lecture at Cornell University in 1966 arranged by my colleague Edwin Salpeter. The speaker was Professor W C DeMarcus and his topic concerned the Great Red Spot of Jupiter. In the course of the lecture I was reminded that this giant planet is 11 times the size of our Earth, yet its average density is not much more than that of water under normal conditions (it is around 1.3 g cm^{-3} or, more interestingly, for what follows about 15 times that of ordinary solid hydrogen). Consistent with this I learned that the constitution of this massive planet was, nine atoms out of ten, composed of hydrogen, in fact close to cosmic abundance. I was also informed that Jupiter was emitting almost twice as much energy as it receives from the sun, indicating a departure from steady state conditions and the likely presence of high internal temperatures. But I think what gripped me most at that time was the statement that Jupiter possessed an extremely high magnetic field suggesting at the very least the possibility of significant circulating currents, putatively in a conducting region of quite considerable extent. The inference I made then, and evidently it was substantially correct, was that given the sheer

size of Jupiter (and also of the companion giant Saturn) there had to be an enormous region of metallic hydrogen present in the planet and if so, metallic hydrogen must then be the most abundant of all condensed substances in our planetary system. It seemed eminently worthy of further study as a fundamental problem in condensed matter physics.

2. Metallic hydrogen and its early alloys

The metallic hydrogen present in Jupiter is, as noted, largely at elevated temperatures, but in a relatively short time after the DeMarcus lecture questions began to raise themselves, including most prominently: what properties might metallic phases of hydrogen have at much lower temperatures, even in a ground state? For example, given that the proton has a mass only 1836 times that of the electron, what forms of order might be taken up by the protons, and what orderings might arise in the electron system as well? The clue from an analysis of Jovian conditions was that these questions should be asked for densities an order of magnitude (at least) higher than is found for hydrogen under normal low-temperature conditions, and for the protons quantum effects could be of prime importance as they almost intrinsically are for the electrons.

Actually the broader study of condensed matter at other than the blithely accidental conditions of one atmosphere appeared to me be a venture of some considerable interest and even useful, though I did encounter those who took a quite opposite view. I was mildly reinforced in my position by a letter I ran across by Fitzgerald [1] (of Fitzgerald contraction) on the very subject of 'The Value of Useless Studies' with a trenchant central remark in it which stated, with measured authority, that '... if the Universities will not study useless subjects, who will?'. In the event, this line of research centred on high-pressure studies has been more than useful and has yielded substantial new physics, as Hemley and Ashcroft [2] have noted. To give a sense of quite remarkable experimental progress over the intervening years, it might be noted that solid hydrogen at low temperatures has been statically compressed by a factor of around 12.2, and it has now been observed to become black (in the visible) [3], indicating that a gap is near closure. And through shock compression, necessarily at higher temperatures, a metallic state has indeed been recorded [4], just as the conditions on Jupiter would suggest.

One of the more ubiquitous forms of electronic order in the metallic state is the occurrence of superconductivity, and towards the end of 1967 I began to piece together three prominent properties of near ground-state metallic hydrogen all favourable for the onset of such a state; the first was the scale of the phonon energies, related of course to the diminutive mass of the proton. In a metallic state an important energy is that set by the plasma frequency of the ions, and in the case of hydrogen this is $\hbar\omega_p = (m_e/m_p)^{1/2} 2\sqrt{3}/r_s^{3/2}$ (rydberg), or $12\,753/r_s^{3/2}$ (K) and under the conditions of interest is gauged by a characteristic energy equivalent of some 4500 K (interestingly close to the vibron energy in the molecule at one atmosphere). The second was that, unlike other metals, the ion in this system possessed no bound or core states that are otherwise so effective in establishing the weak pseudopotential concept, and the electron-ion interaction was therefore likely to be quite strong. If so, then *a fortiori* the effective electron-phonon interaction should also be strong. And thirdly, since the bands were wide, the effects of the direct electron-electron interaction, generally thought then to be inimical to superconducting order (but see below), seemed to be no more damaging than they would be in other electronically dense simple metals. It appeared therefore not unreasonable to investigate the possibility that metallic hydrogen, in monatomic arrangements, might be a viable candidate for quite high-temperature superconductivity. The arguments and estimates based on the BCS theory of the day were presented in a short paper in 1968 [5] along with estimates. Not long

afterwards I discovered that Ginzburg considered the attainment of a metallic state of hydrogen to be one of the key problems in physics and astrophysics, initially in 1971 [6], and recently reaffirmed in a near 30-year reappraisal [7].

Though the prediction of superconducting transition temperatures was known even in the late 1960s to be an exercise fraught with difficulty, a more pertinent obstacle at the time to the notion of a high-temperature superconducting phase of metallic hydrogen was rooted in one of Matthias's pragmatic rules which held sway in those days, namely that no monovalent metal shall be a superconductor (valence 6 was also resolutely excluded from superconductivity by a parallel edict). Further, the prediction of the pressure at which a low-temperature sample of hydrogen might be induced to become metallic was also a far from trivial pursuit. However, for a development to come some years later (and taken up below) I found it quite noteworthy that certain metallic hydrides were superconductors and these hydrides of palladium were especially curious. Thus, PdH_x is a superconductor (for $x > \sim 0.7$) with a transition temperature rising with x ; but PdD_x and PdT_x are also good superconductors and for protium (H), deuterium (D) and tritium (T) there is a remarkable observation that the isotope effect is exactly the opposite of what might be expected from the BCS predictions [8].

It is noteworthy that a 'hydrogen alloy', and in fact the PdH system, arises as an early example of Bridgman's insight on atomic destructibility through an important extension of the concept of 'internally generated pressure'. It presents a case for what we might now view as the mimicking of external pressure by exploiting the compressive tendencies associated with the chemistry of appropriate elements in combination. The notion that significant qualitative changes may take place in hydrogen when it is combined with palladium appear to be first recorded in 1868, by Graham [9]. It was later referred to by Ubbelohde [10] in 1931 as 'Graham's hydrogenium'; Ubbelohde further studied the absorption of hydrogen by palladium and then later (in a paper which refers in its title to metallic hydrogen and its alloys) made the prescient remark that 'The evidence that hydrogen is in the metallic state has been reviewed (in [10]) and may be summarized by the statements that hydrogen dissolves as atoms and at least a portion of these atoms is ionized to give electrons and protons'. (Today the appearance of 'protons' looks odd, but this was before the discovery of the neutron and the realization of the extraordinarily strong binding of nuclei.)

The idea of hydrogen present in a metallic environment, the origin of which may be traced in part to a companion element (whose role may also be seen to provide an additional source for an increase in average electronic density), has a quite modern counterpart. Thus, in terms of the standard linear measure r_s of average inverse electronic density ρ_e (where $(4\pi/3)r_s^3 = 1/\rho_e$), the late-comer superconductor MgB_2 is assigned a value $r_s = 1.81$, where for the constituent Mg it is 2.66, and for this element would therefore represent a factor of 3.2 in average electronic density. I return below to the pursuit of the light elements in combination, and the 'utility' of pre-compression by other constituents.

It is well accepted that a key motivation in the metallic hydrogen problem was the appearance of the paper by Wigner and Huntington [11], in 1935. Hydrogen can be found twice in the periodic table, once in group VII with the halogens, and once in group I, along with the alkali metals. Though the group VII (paired) characteristics have largely governed the accounting for its high-pressure behaviour, it was a possible monatomic form that was treated by Wigner and Huntington. On the assumption that a body-centred-cubic (BCC) lattice would be taken up (as in the other alkalis under ordinary conditions), they found that there was a minimum in the total energy as a function of density. It is at quite high compression, and as we now know it does not survive if, for example, the BCC structure is instead regarded as a simple cubic but with an adjustable two point basis. If this is taken as the cube corner and the cube centre, a BCC is then defined, a Bravais lattice in its own right. But if enthalpy is

first minimized with respect to basis separation the protons are seen to pair, the centre proton moving towards the corner proton, an effect persistently evident in the structures actually taken up by hydrogen (these being far more complex than BCC). Experimentally it is established, primarily through the survival of vibron modes detectable by Raman scattering, that even at relative solid compressions in excess of 12 the pairing of protons remains distinctly evident and indeed their associated dynamics have been a source of considerable information on the insulating state of hydrogen at high pressure.

A paired state of protons necessarily implies an even number of electrons per cell in any static crystalline environment, and in a one-electron viewpoint this satisfies the necessary requirement for insulating behaviour. Sufficiency requires that for ever-increasing density no band overlap may occur. However, the acceptance of this as an eventual possibility leads to the possibility of a paired metallic structure in dense hydrogen, a state first considered by Ramaker *et al* [12] and soon after with a band-theoretical approach by Friedli and Ashcroft [13]. The exchange-driven pairing terms seem sufficiently strong in hydrogen (traceable in part to the enduring consequences of the cusp condition) to survive the effects of screening expected upon passage into the metallic state. Quite some years later it became apparent that a paired metallic state could be even more favourable for the appearance of high-temperature superconductivity [14] in metallic hydrogen. It now seems that there may even be a small range of densities, these corresponding to conditions where protons are just on the verge of despairing, where Feshbach resonance conditions may be prevailing, and where very substantial superconducting transition temperatures may occur [15].

3. Pressure and emergent electronic structure

Given the scale of compressions now achievable both statically and dynamically it is apparent that the role of pressure can be considerable in attaining a more comprehensive understanding of condensed matter and its orderings [2]. Systematic densification obviously alters electronic structure but the latter is also deeply interconnected with the real space structure, a quite general consequence far transcending hydrogen of course. One early case demonstrating significant pressure-induced changes in electronic structure, notable for its occurrence in a so-called 'simple metal', concerned aluminium and its optical properties [16]. These revealed very significant progressions in the interband absorption, important because they unambiguously fixed [17] the hitherto undetermined sign of one of the principal components of the electron-ion pseudopotential determined from Fermi surface measurements [18]. However, they not only established the sign as positive, but also that the magnitude *increased* notably with pressure.

This behaviour looked somewhat innocuous but it actually held in it the seeds of an idea to be advanced quite a bit later. For it occurred to me that the positivity of the pseudopotential could be related to a probing (increasing ever further with pressure) of the inner and repulsive, regions of the core of the ions. Thus when in late 1997 proposals were being sought for candidate experiments for the proposed high-pressure line of the Advanced Photon Source it seemed not implausible to suggest that the new capabilities might be brought to bear on the light elements but under conditions where the core effects would become of increasing physical relevance. For under such conditions it was far from clear to me that the familiar lore in high-pressure physics, that systems would become increasingly close packed with density, would necessarily prevail, even in what might be regarded as traditionally 'simple' systems from the structural viewpoint.

In searching for initial manifestations of this potentially new physics it is clear that significant changes in near neighbour separations are a *sine qua non* and the systems of interest (largely the s-p systems) invariably have low compressibilities. The most favourable

case appeared to be lithium, and the subsequent theoretical investigations of Neaton and Ashcroft [19] showed that at around 40 GPa a profusion of quite complex structures became competitive, and also that at considerably higher pressures it might also be possible for lithium to adopt, in its ground state, a paired structure. Another prediction was related to an interesting and direct manifestation of the pressure-impelled involvement of core-physics, namely a narrowing of the valence band with pressure. This implies a rising electronic density of states which, when coupled with the inexorable rise of the electron-ion interaction (and hence the electron-phonon interaction), led of course to a suggestion [19] that at high pressures lithium could well be a candidate for superconductivity (but once more in conflict with Matthias's rule). Calculations based on MacMillan's approximate solutions to the Eliashberg equation [20] confirmed that indeed lithium could well be a superconductor and with relatively high transition temperatures. The experiments of Hanfland *et al* [21] reported very interesting complex structures around 40 GPa with further calculations also suggesting the onset of a paired structure, but a much higher pressures (around 165 GPa) than initially found in [19].

That compressed lithium could exhibit superconductivity was established in fairly short order by Shimizu and co-workers [22] originally indicating transition temperatures rising close to 20 K. Subsequently, Struzhkin *et al* [23] observed a variance in T_c with pressure clearly indicative of structural phase transitions. In a very recent paper Deemyad and Schilling [24] have succeeded in measuring the superconducting transition temperature under near hydrostatic conditions with a tantalizing rise of T_c near 66 GPa, yet curiously followed soon thereafter by what appears to be a disappearance of a measurable T_c . Clearly the physical character of the states of lithium near these compressions becomes an issue of some importance. Certainly the behaviour of the lithium under shock compressions supports a significant departure of otherwise nearly free electron characteristics [25, 26]. An obvious extension of these notions to sodium [27], and to sodium-lithium alloys, especially stoichiometric arrangements, seems warranted. Since at one atmosphere these systems conform reasonably well to the requirements of a pseudopotential description, but at higher densities on-site repulsions are evidently becoming significant, the role of pressure is to tune between the Hubbard-pseudopotential limits, something that had been raised as a very interesting possibility by Siringo *et al* [28].

4. Dynamical effects, and the light elements in combination

In terms of the familiar one- and two-particle density operators ($\hat{\rho}_\alpha^{(1)}(\mathbf{r})$ and $\hat{\rho}_\alpha^{(2)}(\mathbf{r}, \mathbf{r}')$), what we might view as quantum-mechanical observables (the one- and two-particle densities) for problems in condensed matter physics, the hydrogen and lithium starting Hamiltonians are of course similar; thus for hydrogen

$$\hat{H} = \hat{T}_p + \hat{T}_e + \frac{1}{2} \int_V \mathbf{dr} \int_V \mathbf{dr}' v_c(\mathbf{r} - \mathbf{r}') \{ \hat{\rho}_p^{(2)}(\mathbf{r}, \mathbf{r}') - 2\hat{\rho}_p^{(1)}(\mathbf{r})\hat{\rho}_e^{(1)}(\mathbf{r}') + \hat{\rho}_e^{(2)}(\mathbf{r}, \mathbf{r}') \}$$

while for lithium

$$\hat{H} = \hat{T}_n + \hat{T}_e + \frac{1}{2} \int_V \mathbf{dr} \int_V \mathbf{dr}' v_c(\mathbf{r} - \mathbf{r}') \{ 9\hat{\rho}_p^{(2)}(\mathbf{r}, \mathbf{r}') - 6\hat{\rho}_p^{(1)}(\mathbf{r})\hat{\rho}_e^{(1)}(\mathbf{r}') + \hat{\rho}_e^{(2)}(\mathbf{r}, \mathbf{r}') \}$$

where $v_c(r) = e^2/r$ is the fundamental Coulomb interaction. Since we are dealing with light elements the kinetic energy of the nuclei (\hat{T}_p or \hat{T}_n) can be very significant. In particular this significance has to be assessed in terms of the effective interactions governing the dynamics of the more massive degrees of freedom. In the case of hydrogen, the cusp condition, mentioned above, very much constrains the localization of electronic charge within a significant fraction of a Bohr radius from a proton. A consequence is a certain invariance in the behaviour of the effective proton-proton interaction at proton separations also on the scale of a Bohr radius.

This stands in some contrast to the behaviour at larger separations, which at low densities is sufficiently attractive to cause the strong proton pairing characteristic of the molecular phase. Yet, there is a gradual evening-out of the electron density with pressure where charge localized in this 'molecular bond' finds its way to interstitial regions and is then accompanied, unsurprisingly, by an equally systematic reduction in the attractive region of the proton pairing interaction.

But there is little change in the short-range contribution, as noted, and this may have exceedingly interesting physical consequences. For, through propitious choice of density, the formerly attractive region can be brought to within dynamic energies of the protons, and throughout a significant fraction of an average cell the confluence of these energies is not significantly different from the situation faced in helium under normal conditions, these leading to a persistence of its fluid state to the lowest of temperatures. These elementary arguments, flowing from basic properties of dense hydrogen, then lead first to the expectation of a maximum in the melting curve [29] (some hint of this perhaps already occurring in the measurements of Datchi *et al* [30]). But, second, there is also the possibility that hydrogen (and by similar arguments, deuterium also) will take up a ground state fluid phase. This will be a new phase of matter, namely a ground state liquid metal, at least over a range of density, and its subsequent quantum orderings are suggested to be richly complex [31]. Spatially the fluid state is expected to be isotropic, in contrast to liquid crystal like phases that had arisen earlier as possible ground states [32]. Given that the interaction can be brought into a region of instabilities (for protons, deuterons and electrons) the tuning of the couplings with pressure may reveal very significant orderings.

5. Bridgman's legacy

In terms of future directions concerning the legacy of Bridgman's atomic and molecular destructibility it would also appear that the light elements in combination may have much to offer. Given the recent experience with lithium and its reported superconductivity at temperatures which are considerable, it is of some interest to consider a pathway via systems that may be viewed perhaps as intermediate in the quest for metallic hydrogen itself, that is, hydrogen in combination with light elements. Soon after the appearance of the suggestion that metallic hydrogen could well be a high-temperature superconductor, it was proposed that a hydride (containing lithium and fluorine) might also be in contention for superconductivity in a metallic state [33].

The underlying physics that may make these systems attractive is simply based on the observation that some prior densification of hydrogen is clearly being achieved chemically, through the presence of other constituents. If so then surely an essential proposition is to consider metallic phases of systems that are as hydrogen rich as may be found. The notion to pursue hydrogen-rich systems arose earlier in the context of the hydrides of boron [34], since the latter had been shown to be a good superconductor in its own right, as soon as it is impelled to enter the metallic state [35]. A clear extension, which increases the hydrogen content further, is to consider the group IVa hydrides and also carefully chosen mixtures of these. Lead is a strong-coupling superconductor. Plumbane (PbH_4) is marginally stable, but nevertheless an interesting case for experimental study at high density. Stannane is considerably more stable, and has a high linear dipole polarizability. Germane (GeH_4) is quite stable, and likewise has an especially high linear dipole polarizability indicating through the Goldhammer–Herzfeld criterion a possible metallic transition at reasonably modest densities [36]. Silane (SiH_4) also should have a metallic transition at pressures readily achievable in a diamond cell. But perhaps the most interesting case of all will be metallic methane, CH_4 [37]. If A is the mass

number of the group IVa element, then the longitudinal plasmon frequency that will be in evidence when a metallic state is formed converts to an energy (the parallel of the hydrogen case above) which is given by $(m_e/m_p)^{1/2}(8/\{A + 4\})^{1/2}2\sqrt{3}/r_s^{3/2}$ (rydberg). In the case of CH₄ this yields $9016/r_s^{3/2}$ (K). Though screening will lower the corresponding phonon frequencies, this is clearly a substantial energy scale. The basic arguments advanced above suggesting that hydrogen will be a high-temperature superconductor also apply here, and as has already been mentioned the phonon energy scale is quite competitive in some cases. The main point, however, is that to enter the metallic states of these hydrides will require pressures far less than expected for pure hydrogen at equivalent densities. An interesting experimental issue is whether such hydrides might be incorporated as a subsystem in a greater unit cell, the whole providing the requisite chemical pre-compression (but under ambient conditions) for maintenance of a metallic and superconducting state. Such a discovery could be seen as an enduring tribute to the remarkable insight of Percy Bridgman as well as to the field of high-pressure physics where he provided so many remarkable contributions.

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