Approaches for Reducing the Insulator-Metal Transition Pressure in Hydrogen

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Two possible techniques for reducing the external pressure required to induce the insulator-metal transition in solid hydrogen are described. One uses impurities to lower the energy of the metallic phase relative to that of the insulating phase. The other utilizes a negative pressure induced in the insulating phase by electron-hole pairs, created either with laser irradiation or pulsed synchrotron sources.

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The quest to synthesize a high-pressure metallic phase of hydrogen is motivated both by the fundamental interest of this "simplest" metal, and by some of its predicted useful properties, such as a very high superconducting transition[1,2] T_c. Unfortunately, the corresponding predicted insulator-metal transition pressures, varying from 100 to 1000 GPa in recent estimates,[3] are mostly above the range of pressure currently available in a static diamond-cell apparatus. For this and other reasons chemical techniques for simulating the dissociative effect of external pressure have been suggested, such as the use of a proposed artificial compound LiH_2F in the place of pure hydrogen.[4] In this Letter we speculate on the applicability of two as yet untried techniques which may also simulate the effects of external pressure. Both are based on the general observation that at least part of the energy favoring insulating phases of elements and compounds can be linked to the presence of an energy gap between filled and empty electron states.[5] It follows that processes which locally reduce the gap (such as impurity or defect production), or reduce the *effects* of the gap (such as electron-hole pair creation), should favor the metallic phase.

(a) Impurity stabilization.—It has been known for some time that impurities can have a destabilizing effect on semiconducting phases of solids. For example, a concentration of donor impurities as low as 0.1% can cause a 5% reduction in certain shear elastic constants of Si and Ge.[6] Furthermore, it has been observed[7] that the equilibrium 2×1 reconstructed Si surface, which is semiconducting, can be destabilized by the addition of 0.01–0.05 monolayers of Te. In addition, we note that impurities can stabilize superconducting compounds which are *not* stable in their pure forms, such as[8] $A15$ Nb_3Nb.

The effect of impurities on the relative stability of the two phases of hydrogen under discussion is conveniently discussed in terms of their associated screening functions. The impurity screening energy in the metallic phase is expected to be larger than that in the insulating phase, because of the nonvanishing Fermi-level density of states in the former. To obtain an estimate of the magnitude of the energy difference, we consider a trivalent impurity modeled by an empty-core pseudopotential (a valence of three is chosen because we consider this to be the approximate limit of applicability of the linear screening theory to be used). Thus $V_{imp} = -(4\pi Ze^2/q^2)\cos qr_c$ for some core radius r_c. The impurity screening energy is then given to second order in V_{imp} by

$$E_{scr}^{met,\,ins} = -e^2/\pi \int_0^\infty dq[1 - \epsilon_{met,\,ins}^{-1}(q)]\cos^2 qr_c\,, \qquad (1)$$

where $\epsilon_{met,\,ins}$ are the metal and insulator static dielectric functions. We take $\epsilon_{met}(q) = 1 + k_s^2/q^2$ and[9]

$$\epsilon_{ins}(q) = 1 + (\epsilon_0 - 1)/[1 + \epsilon_0(q^2/k_{ins}^2)]\,,$$

where k_s is the Thomas-Fermi wave vector, $k_{ins}^2 = k_s^2\epsilon_0/(\epsilon_0 - 1)$ (both phases are taken to have the same density for ease of comparison), and ϵ_0 is the insulator's static dielectric constant. It is obtained approximately from the band-structure calculations of Ref. 10, by use of the formula[11] $\epsilon_0 = 1 + \omega_p^2/E_g^2$, where E_g is the average direct gap and ω_p is the plasma frequency. At $r_s = 1.75$, a density roughly corresponding to the highest pressures currently used in diamond-cell experiments, and with $r_0 = 1.1$ a.u. corresponding to[12] Al, we have $\epsilon_0 = 7$ and $E_{scr}^{met} - E_{scr}^{ins} = -5$ eV. At this density, the calculated energy difference[13] between the semiconducting phases is roughly 1 eV. Thus for a 10% concentration of impurities, about half of this energy difference can be elim-

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inated, and correspondingly the structural transition pressure is reduced substantially.

Existing band-theoretic techniques are not sufficiently accurate or flexible to point to the optimal impurity for stabilizing the metallic phase. However, we regard transition-metal impurities to be good choices, for two reasons: (1) Transition-metal surfaces are known to effectively dissociate hydrogen molecules. A transition-metal impurity in a hydrogen matrix might then be thought of as a small region of transition-metal surface in contact with the surrounding hydrogen atoms. (2) Some transition metals are known to form very hydrogen-rich compounds, such as YH_3. In these compounds the hydrogen atoms generally are found in a metallic crystal structure, and characteristic hydrogen-associated bands are found below the transition-metal d bands.[14] Their superconducting properties are dissimilar to those predicted for metallic hydrogen because the density of transition-metal atoms is large. Accordingly, the electrons they contribute raise the Fermi level above the hydrogen bands into a gap between these and the transition-metal d bands, or into the d bands themselves. If it were possible to synthesize a compound with a lower relative density of transition-metal atoms, then the hydrogen atoms could maintain their metallic crystal structure with the Fermi level staying *inside* the hydrogen-associated bands. Such a compound might be created by first implanting a solid H_2 matrix with transition-metal ions, and subsequently applying external pressure. Alternatively, the physical mixing of a hydride with pure hydrogen might be attempted. Both of these techniques have the desirable feature that they produce large numbers of defects, and these are also expected to favor the metallic phase by the screening-energy arguments presented above.

Even if the impurities do not stabilize the metallic crystal structures, they are expected to contribute carriers to the molecular phase, provided the band gap is not too large. For electropositive impurities such as Cs, it is very likely that these will be conduction-band electrons. Two of the features responsible for the predicted high T_c of the metallic phase,[1] namely, the high characteristic (Debye) frequency and the large electron-phonon coupling, are present in the molecular phase as well. If a sufficiently large impurity concentration can be incorporated, then the Fermi-level density of states in the defected molecular phase may also be high, and it is then possible to tune the Fermi level to coincide with peaks in the density of states. Thus the molecular phase itself can, in principle, support a superconducting transition. In this regard, we note that the superconductivity in semiconductors with only ~ 0.02 carriers per atom has been both predicted[15] and observed.[16]

(b) Electron-hole pair creation.—It is known that the laser annealing process, involving intense irradiation of semiconductors with photons at energies above the band-gap energy, can result in large-scale structural rearrangements.[17] We propose that similar techniques may also be used to help synthesize the metallic phase of hydrogen by reducing the pressure required to compress the molecular phase. For the photons to reach the hydrogen and be absorbed, the band gap E_g^{H} of the molecular hydrogen must be smaller than the gap E_g^{dia} of the diamond cell itself. This is not the case at zero pressure, where $E_g^{\text{H}} = 14.5$ eV (Ref. 18) and $E_g^{\text{dia}} = 5.4$ eV.[19] However, E_g^{H} will drop much more rapidly than E_g^{dia} with pressure, because of the large compressibility of the hydrogen. Using the calculations of Ref. 10 for the volume dependence of E_g^{H}, the molecular hydrogen equation of state of Ref. 13, and the pressure dependence of E_g^{dia} reported in Ref. 19, we find coincidence in the band gap, i.e., $E_g^{\text{H}} = E_g^{\text{dia}} = 5.0$ eV, at $P \simeq 30$ GPa.

The usual picture of the transition to the metallic crystal structure in hydrogen involves a substantial reduction of the band gap, followed by a structural transition at a pressure P_{st}. It is not known whether the structural transition occurs before or after the bands overlap in the diatomically ordered structure (at a pressure P_{bo}, say). The presence of a concentration x of electron-hole pairs is expected to shift the equation of state of the molecular phase by an amount equal to $p^{\text{e-h}} = -x(dE_g^{\text{H}}/d\Omega_{\text{at}})$, where Ω_{at} is the volume per atom. Since E_g^{H} drops with compression, $p^{\text{e-h}} < 0$. Using the $E_g^{\text{H}}(\Omega_{\text{at}})$ values calculated in Ref. 10, we find a maximum value of $dE_g^{\text{H}}/\Omega_{\text{at}}$ equal to approximately 700 GPa, at the band-overlap transition.

This means that if it is possible to obtain a 5% concentration of electron-hole pairs, an equivalent excess pressure of roughly 35 GPa could be obtained. The resulting effect on the pressure required to induce the structural transition depends on whether P_{st} is greater or less than P_{bo}. If $P_{\text{st}} > P_{\text{bo}}$, then P_{st} is essentially unaffected by the presence of the electron-hole pairs, since $P^{\text{e-h}}$ vanishes along the trajectory leading from

the band-overlap transition to the metallic crystal structure. However, if $P_{bo} < P_{st}$, then the external pressure required to compress the diatomic phase to the volume at which the structural transition occurs is reduced by an amount $|P^{e-h}|$. Furthermore, the energy of the molecular phase at a given volume is raised relative to that of the metallic phase by the electron-hole pairs. Therefore we expect the structural transition to occur at a pressure less than $P_{st} - |P^{e-h}|$.

It might be argued that as soon as the transition to the monatomic crystal structure occurs, the electron-hole pairs will recombine, and if $P < P_{st}$ the solid will immediately revert to the molecular crystal structure. Here we argue the importance of kinetic considerations. It has been known for some time that nonequilibrium metallic phases of certain III-V semiconductors can be metastable at liquid-nitrogen temperatures, even at zero external pressure.[20,21] Furthermore, the insulating phase may nucleate and actually grow less rapidly than the metallic phase. Such an effect is seen, for instance, at the α-β transition in Sn (Ref. 22) and even possibly at the metal-insulator transition in VO_2, which shows an asymmetry in the growth rates of the metallic and insulating phases in dynamic heating experiments.[23] If nucleation is centered around defects, then the arguments presented above on screening energies would suggest that, other factors being equal, the nucleation of the metallic phase is favored. Finally, if it is possible to obtain pressures greater than P_{st} in the laboratory, but nucleation and growth of the metallic phase are insufficiently fast, then it can be accelerated by the presence of electron-hole pairs.

Achieving a sufficiently high density of electron-hole pairs in hydrogen will be a difficult experimental challenge, but a possible approach is to use a very short burst of very high intensity radiation, as in the usual semiconductor laser annealing process. For high enough external pressures, the hydrogen band gap will be of a scale that a readily available laser in the 2-eV range can be used. At lower pressures, a frequency doubler together with a focusing arrangement to increase the incident power density is immediately suggested. Alternatively, a color-center laser might match the appropriate interband absorption edge. The effectiveness of this approach hinges on the ratio of the lifetime of the electrons and holes produced to the time required for the structural transition to take place, neither time being known accurately. However, we observe that room-temperature recombination times in semiconductors range from 10^{-3} to 10^{-8} sec,[24] and that martensitic phase transformations have been observed to nucleate in times as short as 10^{-7} sec, with subsequent growth at a rate of 10^5 cm/sec.[25]

A second possibility is the use of pulsed radiation from a synchrotron radiation source. Assuming an absorption length of 1 μm, an external pressure sufficient to reduce the band gap to 1 eV, and using a favorable electron-hole recombination lifetime of 10^{-3} sec, we find that the incident power intensity required to maintain an electron-hole pair density of 5% is of order 10^4 W/cm^2. It should be noted in this regard that the heat supplied to the sample through the use of these techniques is expected to lower the structural transition pressure, simply because the metallic crystal structure has greater entropy than the diatomic one. This effect has been observed in the semiconductor diamond to β-tin structural transitions, in which the transition pressure is typically reduced by roughly 20% at the melting temperature.[5]

We conclude by observing that the feasibility of the techniques described above depends crucially on parameters whose values we are unable to calculate precisely. For this reason, it might be useful to develop the techniques suggested in systems whose transition pressures are currently in the experimentally attainable range. One such system is I_2, which is believed[26] to have a second-order band-overlap transition at 18 GPa, and a subsequent first-order transition at 21 GPa. Br_2 and Cl_2 are expected to have similar transitions at higher pressures, which are still in the experimentally accessible range. Another useful precursor experiment is the investigation of effects of the dopant impurity concentration on the diamond to β-tin transition pressures in semiconductors, these ranging from roughly 0 to 25 GPa. Although the effects have generally been assumed to be small, it may be possible to obtain observable effects with the use of modern ion implantation techniques, which allow the dopant concentration to greatly exceed its equilibrium value.[27]

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