

Hydrogen Dominant Metallic Alloys: High Temperature Superconductors?

N. W. Ashcroft

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501, USA

Donostia International Physics Center, San Sebastian, Spain

(Received 29 December 2003; published 6 May 2004)

The arguments suggesting that **metallic hydrogen**, either as a monatomic or paired metal, should be a candidate **for high temperature superconductivity** are shown to apply with comparable weight to **alloys of metallic hydrogen** where hydrogen is a dominant constituent, for example, in the dense group IVa hydrides. The attainment of metallic states should be well within current capabilities of diamond anvil cells, but at pressures considerably lower than may be necessary for hydrogen.

DOI: 10.1103/PhysRevLett.92.187002

PACS numbers: 74.10.+v, 71.30.+h

Recent observations of superconductivity in lithium at high pressures [1–3] with transition temperatures T_c rising as high as 15 K appear to suggest that experimental interest in the possibility of superconductivity in systems involving the light elements at high densities may be well merited. The extension to the light elements in combination has been potently illustrated with the discovery of superconductivity at impressively high temperatures in MgB_2 [4], a system with eight electrons per unit cell and in overlapping bands. In metallic form the lightest of all elements, hydrogen, is predicted to be a superconductor [5] with high transition temperatures in monatomic structures and even higher in structures where, in band-overlap states, protons retain their pairing [6]. As potential superconductors hydrides have also been raised in the past [7] for moderate or relatively low hydrogen content. The point in what follows is to consider eventual metallic and superconducting states of mainly covalent metallic hydrides, with even larger hydrogen content. It will be illustrated in group IVa hydrides where for simple structures, there are again eight electrons per unit cell. In such combinations a critical observation is that in a chemical sense hydrogen has already undergone a form of “precompression” [8] and that once impelled by further external pressure to enter a metallic phase the electrons from both the hydrogen and the group IVa element may participate in *common overlapping* bands. Individually tin and lead are both superconductors, as are germanium and silicon once impelled by pressure to enter the metallic state.

The central physical feature of these systems is to be found in the scales of energies associated with their lattice dynamics. They are exceedingly high for the less massive protons (as in metallic hydrogen) but there are also lower frequency branches for the more massive ions, these having much higher charges and leading also to ostensibly stronger electron couplings. As sole constituents they might well conform to strong-coupling superconductors with phonons as exchange bosons. The overlapping bands of the compressed hydrides will be wide, the density of states generally high, and the electron-ion interactions,

from protons and group IVa ions, significant. Under conditions of density where these systems would be described as wideband insulators, or even semiconductors, simple structures can lead to complete occupancy of four bands, as would be the case in MgB_2 . It is clear that subsequent attainment of a band-overlap state of contiguous bands will lead to a compensated metal with a Fermi surface in several zones, an important point for what follows since this circumstance favors significant contributions from umklapp (or interband) terms arising from the electron-phonon coupling. Because of the dominance of umklapp processes in this problem, the well known difficulty of dealing quantitatively with these will eventually necessitate more detailed assessments than are given here.

Given the wideband character of the metallic phases, the Morel-Anderson or Coulomb pseudopotential μ^* entering into approximations for the superconducting transition temperature is also expected to be favorable for the onset of a superconducting phase, and especially so if the structures taken up promote formation of a compensated metal (an even number of electrons per unit cell is mandated). The arguments supporting metallic hydrogen as a possible candidate for high temperature superconductivity should therefore carry through as well for these hydrides but possibly with an additional physical boost from the lower mode frequencies and the further possibility of tuning them to values that are optimal in pursuit of higher T_c 's. In terms of required pressures the onset of the metallic phases may well occur at values considerably lower than are required to drive hydrogen metallic, as will be seen.

Let r_s be the standard measure of the average valence electron density for a system. Some important dynamical energy scales can now be set; first, the proton plasmon energy for a metallic state of hydrogen is (in Rydbergs) $\hbar\omega_{p,p} = (m_e/m_n)^{1/2} 2\sqrt{3}/r_s^{3/2}$. Here m_n is the mass of the nucleon, m_e the mass of an electron, and $\hbar\omega_{p,e}$ the plasmon energy for electrons. Second, for a group IVa hydride the equivalent energy for an acoustic plasmon, when Am_n is the mass of the nucleus involved, is (in Rydbergs) $(m_e/m_n)^{1/2} 2\sqrt{3} [8/(A+4)]^{1/2}$, and for germane, for

example, at a possible metallic transition in the vicinity of $r_s = 1.71$ (see below) this leads to 1840 K. This energy translates into a somewhat lower scale when screening is incorporated (as originally noted by McMillan [9] in the context of strong-coupling superconductors and alloys) as it also does in metallic hydrogen itself, but to a lesser extent. Third, in the dense hydride there is also a characteristic optical plasmon energy for the proton subsystem. If the ions are regarded as massive, and further that in a long wavelength limit their charge is taken to cancel half that of the standard background, then this energy is just $(m_e/m_n)^{1/2} \sqrt{6}/r_s^{3/2}$ (again in Rydbergs), and though lower than that for protons alone at an equivalent density it remains very substantial.

The essential dimensionless quantities entering approximate solutions for T_c (of the linearized Eliashberg equations) are λ , which embodies the attractive effects of the electron-phonon coupling, and μ^* which accounts for the generally repulsive effects of direct Coulomb interactions between electrons. Scales can also be set for λ and μ^* for a one-component system using elementary arguments; thus, if V_c is the Coulomb interaction, then in a BCS viewpoint a measure of repulsive effects is $\mu = \langle N_0 V_c(\mathbf{k}' - \mathbf{k}) \rangle$ the average being taken over a spherical Fermi surface (diameter $2k_F$). Here N_0 is the density of states per unit volume for a given spin, evaluated at the Fermi energy [it may be written as $(1/4\pi^2)k_F^3/\epsilon_F$]. If screening is treated in the Thomas-Fermi approximation, and wave vectors normalized to $2k_F$ [$\mathbf{x} = \mathbf{k}/2k_F$, and $(k_0/2k_F)^2 = \gamma = (4/9\pi^4)^{1/3}\tau_s$, where k_0 is the Thomas-Fermi wave vector], then

$$N_0 V_c(\mathbf{x} - \mathbf{x}') = (\gamma^2/2)/[(\mathbf{x}' - \mathbf{x})^2 + \gamma^2], \quad (1)$$

the average of (1) over a sphere of unit diameter then giving $(\gamma^2/2) \ln(1 + 1/\gamma^2)$. With the inclusion of retardation effects (Coulomb couplings propagate far faster than ion dynamical equivalents) the estimate for μ^* then follows from [10]

$$(1/\mu^*) = [(\gamma^2/2) \ln(1 + 1/\gamma^2)]^{-1} + \ln(\hbar\omega_{p,e}/\hbar\omega_p), \quad (2)$$

where $\hbar\omega_{p,e}$ is the electron plasmon energy (see above) and $\hbar\omega_p$ is the corresponding quantity for the ions. Equation (2) then yields the well known values $\mu^* \sim 0.1$; for μ itself the figure is 0.2.

In order to attain a superconducting instability, Eq. (1) must be overcome by the attractive contributions, $\langle N_0 V_{ph} \rangle = \lambda$, originating with screened electron-phonon coupling $g_{\mathbf{q}}(\mathbf{k}', \mathbf{k})$ associated with the scattering of an electron from \mathbf{k} to \mathbf{k}' , by a phonon of wave vector \mathbf{q} . In this case the average is required of $-N_0 2|g_{\mathbf{q}}(\mathbf{k}', \mathbf{k})|^2/\hbar\omega(\mathbf{k}' - \mathbf{k})$ where for a Debye spectrum and longitudinal modes

$$g_{\mathbf{q}}(\mathbf{k}', \mathbf{k}) = \frac{4\pi e^2 f(\mathbf{k}', \mathbf{k})}{[(\mathbf{k}' - \mathbf{k})^2 + k_0^2]} i(\mathbf{k}' - \mathbf{k}) \left(\frac{\hbar}{2cq} \frac{N/V}{Am_n} \right)^{1/2}. \quad (3)$$

In (3) the actual sound speed c is written as $c = \alpha v_F (3m_e/ZAm_m)^{1/2}$, the role of the dimensionless α being to correct the standard Bohm-Staver estimate. The quantity $f(\mathbf{k}', \mathbf{k})$ (generally nonlocal) embodies a pseudopotential correction to the familiar point-ion result. Then for *normal* intraband ($\mathbf{k}' - \mathbf{k} = \mathbf{q}$) processes, the contribution to $\langle N_0 V_{ph} \rangle$ follows from an average on a sphere of unit diameter (but with the restriction $q = |\mathbf{k}' - \mathbf{k}| < k_D$, also normalized) of

$$-N_0 V_c(\mathbf{x} - \mathbf{x}') \left\{ \frac{f^2(\mathbf{x}', \mathbf{x})}{\alpha^2} \frac{\gamma^2}{(\mathbf{x}' - \mathbf{x})^2 + \gamma^2} \right\}. \quad (4)$$

The quantity α is < 1 , and when densities are high f increasingly reflects the short range repulsive region of the pseudopotential, which can become appreciable [11]. Direct comparison with (1) then shows that depending on the system the phonon mechanism may well prevail, but that inclusion of umklapp terms ($\mathbf{k}' - \mathbf{k} = \mathbf{q} + \mathbf{K}$, with \mathbf{K} a reciprocal lattice vector) can increase the contribution from (4) considerably. The importance of umklapp or interband scattering effects in normal-state transport properties is well known [12], and the fact that there are at least four bands involved in this problem (with a Fermi surface in many zones) is now seen to be an extremely propitious feature. (As noted a similar situation prevails in MgB_2 .) From the definition of N_0 (and for NZ electrons in a volume V), it also follows that $|g_{\mathbf{q}}(\mathbf{k}', \mathbf{k})|^2 \sim (V/ZN)(\epsilon_F \hbar\omega_D)$, and g is therefore proportional to the geometric mean of the electron and phonon energy scales. Depending on pressure the former can be 20 eV and above, while the latter can reach 0.2 eV. The coupling is therefore large and, again depending on the system, the phonon term $\lambda = \langle N_0 V_{ph} \rangle$ can reach the strong-coupling values ~ 1 .

When the problem is recast as a search for approximate solutions of the Eliashberg equations the phonon-exchange term (3) is written more generally by utilizing the phonon spectral function $\alpha^2 F(\omega)$ (see [10]) in terms of which the phonon-exchange parameter, λ , is now given by $\lambda = \int_0^\infty d\omega 2\alpha^2 F(\omega)/\omega$, and this quantity also determines the enhancement (beyond band-structure and electron-electron contributions) of the normal-state electronic specific heat [13]. In McMillan's initiating approximate solution [9] for T_c , λ (and μ^*) appear in the well known relation

$$k_B T_c = (\langle \hbar\omega \rangle / 1.2) \times \exp\{-1.04(1 + \lambda)/[\lambda - \mu^*(1 + 0.62\lambda)]\}, \quad (5)$$

where μ^* has often been taken to have the somewhat ubiquitous value of 0.13 (actually quite close to the

estimates provided above, but see below). Similar forms can also incorporate spin fluctuations when physically relevant. The important prefactor in (5) is a characteristic average of the phonon energies originally taken by McMillan to be close to the Debye energy and, to repeat, this will be especially large for the proposed metallic hydrides. Other quite accurate approximations for T_c have been provided by Allen and Dynes [10] and by Wu *et al.* [14], who also summarize exact and series-based solutions for T_c of the Eliashberg equations. It is also known [10] that for large $\lambda k_B T_c \lesssim 0.18\sqrt{\lambda(\hbar\omega)^2}$ where, for example, the measured T_c of lead is only a factor of 2 below this estimate. From this it is apparent that if the metallic group IVa hydrides are in the strong-coupling class, ($\lambda \sim 1$) as the estimates above would indicate, then given their substantial phonon energies the values of T_c should be significant.

The values found for T_c from (5) are known to be exceedingly sensitive to the determination of λ , and hence to $\alpha^2 F$. This matter has been investigated in some depth by Bergmann and Rainer [15] who determined the actual influence on T_c of the contributing phonon frequencies through the (positive definite) functional derivative $\delta T_c / \delta \alpha^2 F[\omega]$. Evidently the frequencies most effective in bringing about changes in T_c are to be found in the vicinity of $2\pi k_B T_c / \hbar$. This is an important observation (the T_c 's of pure metallic hydrogen are estimated to be in excess of 100 K) since it is likely to have a considerable bearing on the role of the lower modes of the hydrides. A tuning within this domain may well be brought about by extending the binary hydride MH_4 to a ternary, $M_x^{(1)}M_{1-x}^{(2)}H_4$ with considerable flexibility in the choice of the heavy ion masses being evident. The higher domain of frequencies, associated with the protons, will continue to lead to a very significant Debye temperature, T_D , and the importance of this can be assessed by again turning to MgB_2 . Differences are reported in the values for T_D for this system according to whether they are determined from thermodynamic functions or from transport properties. However, a reasonable choice, and probably close to a lower bound, is $T_D \sim 800$ K. For some of the hydrides under discussion here the corresponding Debye temperatures could reach more than 3 times this value.

For single crystals of MgB_2 , it appears that above an impurity or defect background the temperature dependence of the normal state resistivity follows a corrected Bloch-Grüneisen law [16]. The scale of increase is notably high, attesting to considerable general strength of the overall electron-phonon coupling. The same principle applies to the metallic hydrides except that in the case of MgB_2 there are two pseudopotentials (corrections to pointion interactions), whereas in MH_4 there is one; prior to screening the protons present full Coulomb interactions to the valence electrons. A clear experimental test of the scale of electron-phonon coupling, and the prominence of

umklapp scattering, will again be the rapidity of the rise of the low temperature static resistivity.

Of crystalline methane, silane, germane, stannane, and the somewhat unstable plumbane, take germane by way of specific example. Its average valence electron density in the one-atmosphere crystalline phase corresponds to $r_s = 2.53$ (a density already higher than that usually ascribed to the valence electrons of the alkalis and the alkaline earths). As a free molecule it has a linear dipole polarizability $\alpha (= \bar{\alpha} a_0^3)$ of 40.2 a.u. [17] and a measure of internal fluctuational physics. By the Goldhammer-Hertzfeld (GH) criterion for the onset of a polarization divergence in the condensed phase would then be expected to take place at $r_s = \bar{\alpha}^{1/3}/2$ or $r_s = 1.71$ just prior to a transition to a metallic phase; this translates into a relative compression of 3.2. For the general case the compression is easily seen to be $2.68/A\rho_m$ where A is the mass number and ρ_m the mass density (in g/cm³). The GH estimate cannot compete, of course, with full density functional calculations for locating transitions between proposed insulating and metallic structures, but it is known to give quite reasonable first estimates [18], and for germane the essential point is that the projected compression appears well within diamond cell capabilities. The presumption that phonons are the primary intermediaries in the pairing mechanism is something that can be investigated with the isotope effect, which now becomes especially interesting because of systematic deuterations ($GeDH_3$, GeD_2H_2 , GeD_3H , and GeD_4 , and likewise for the carbon equivalents in what follows).

The case of possible superconductivity in metallic methane is especially interesting [19] because it has the most favorable dynamical energy scales overall; the characteristic ionic plasmon energy in this case is $9016/r_s^{3/2}$ in Kelvin (the transition to the metallic state, from the GH criterion, is expected at $r_s = 1.3$). For methane the issue of relative compressions to achieve equivalent conditions in dense hydrogen can easily be illustrated (among these hydrides it will probably present the most significant experimental challenge). For already by ~ 38 GPa methane has been compressed by a factor of 2.94 [20], and this corresponds to an average electron density equivalent to $r_s = 1.54$. The 1 atm density of solid hydrogen corresponds to $r_s = 3.13$, and it follows that the average electron density at 38 GPa in methane is already equivalent to hydrogen at eightfold compression (at around 150 GPa). This illustrates the precompression physics mentioned above as a general feature of metallic hydrogen-rich systems. The higher frequency modes in CH_4 have already been observed to increase with density [20,21].

It has been suggested [22] that a maximum in the melting curve of hydrogen may occur (some indication of which may already have been seen experimentally [23] and also theoretically [24]). The ensuing decline of the melting curve with pressure raises the additional possibility [22,25] that in a range of densities a ground-state

fluid may be the preferred phase with off-diagonal long range order then occurring in *both* the electrons and the protons. Some of these requirements on density may also hold for metallic hydrides, and the interesting question then emerging is whether this may translate either into low eutecticlike features or even into sublattice melting for the protons, the heavy ions remaining ordered. Preceding any liquid phase may well be a phase close to structural instability, and this could also favor higher temperature superconductivity as emphasized for metallic hydrogen by Maksimov and Savrasov [26]. The matter is of some interest for, as noted by Allen and Dynes [10], Eliashberg theory appears to place no bounds on achievable values of T_c . Finally, the arguments above may also hold in systems with somewhat lower hydrogen content [27]. Again, compensated systems appear to be best matched to the general problem of lowering the Coulomb pseudopotential μ^* [28]. However, for these lower hydrides as well as the hydrides considered here an emerging experimental challenge centers on the possibility that these systems might eventually be incorporated as subsystems within greater unit cells, the entire system providing the requisite chemical precompressions (but now under ambient conditions) for maintenance of metallic and superconducting states.

Unknown at present is the sequence of structures and states likely to be taken up by these hydrides upon systematic densification, including the possibility of layered arrangements and the intervention of intermediate phases of a partially ionic or charge-density-wave or even of semimetallic character. The Fermi-level density of states is obviously crucial, but irrespective of the scale of T_c in eventual metallic states, a detailed experimental survey of these relatively simple systems (in electronic terms) may offer a significant test of the theory of strong-coupling superconductivity. The fact that the hydrides discussed here are isovalent with MgB_4 is a property that can be shared by other systems (e.g., LiBC [29]), and it is clear that other examples may be sought.

I thank Dr. A. Bergara, Dr. J. Neaton, and Professor F. J. DiSalvo for discussions, and I thank Professor P. Etchenike (Donostia International Physics Center) for his kind hospitality. This work is supported by the National Science Foundation, Grant No. DMR-0302347.

-
- [1] K. Shimizu, H. Ishikawa, D. Takao, T. Yagi, and K. Amaya, *Nature* (London) **419**, 597 (2002).
 - [2] V.V. Struzhkin, M.I. Erements, W. Gan, H-K. Mao, and R.J. Hemley, *Science* **298**, 1213 (2002).
 - [3] S. Deemyad and J.S. Schilling, *Phys. Rev. Lett.* **91**, 167001 (2003).
 - [4] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, *Nature* (London) **410**, 63 (2001).
 - [5] N.W. Ashcroft, *Phys. Rev. Lett.* **21**, 1748 (1968).

- [6] C. F. Richardson and N.W. Ashcroft, *Phys. Rev. Lett.* **78**, 118 (1997).
- [7] For example, J.J. Gilman, *Phys. Rev. Lett.* **26**, 546 (1971); A.W. Overhauser, *Phys. Rev. B* **35**, 411 (1987); R.J. Wijngaarden *et al.*, *J. Alloys Compd.* **308**, 44 (2000).
- [8] In MgB_2 , for example, the average electron density exceeds that of Mg under normal conditions by a factor of 3.2.
- [9] W.L. McMillan, *Phys. Rev.* **167**, 331 (1968).
- [10] P.B. Allen and R.C. Dynes, *Phys. Rev. B* **12**, 905 (1975).
- [11] A clear example of this may be seen in the case of compressed lithium where primary band gaps on the zone faces rapidly exceed the bandwidth itself. See J.B. Neaton and N.W. Ashcroft, *Nature* (London) **400**, 141 (1999).
- [12] J.M. Ziman, *Proc. R. Soc. London* **A226**, 436 (1954); J.M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960).
- [13] N.W. Ashcroft and J.W. Wilkins, *Phys. Lett.* **14**, 785 (1965).
- [14] H-S. Wu, Z-Y. Weng, G. Ji, and Z-F. Zhou, *J. Phys. Chem. Solids* **48**, 395 (1987).
- [15] G. Bergmann and D. Rainer, *Z. Phys.* **263**, 59 (1973).
- [16] J.M. Rowell, *Supercond. Sci. Technol.* **16**, R17 (2003).
- [17] K.R. Mountfield and R.D. Weir, *J. Chem. Phys.* **69**, 774 (1978).
- [18] T.A. Grzybowski and A.L. Ruoff, *Phys. Rev. Lett.* **53**, 489 (1984).
- [19] A. Bergara, J.B. Neaton, and N.W. Ashcroft (unpublished).
- [20] S. Umemoto, T. Yoshii, Y. Akahama and H. Kawamura, *J. Phys. Condens. Matter* **14**, 10675 (2002).
- [21] P. Hebert, A. Polian, P. Loubeyre, and R. Le Toullec, *Phys. Rev. B* **36**, 9196 (1987).
- [22] N.W. Ashcroft, *J. Phys. Condens. Matter* **12**, A129 (2000).
- [23] F. Datchi, P. Loubeyre, and R. Le Toullec, *Phys. Rev. B* **61**, 6535 (2000).
- [24] S. Bonev *et al.* (to be published).
- [25] N.W. Ashcroft, in *High Pressure Phenomena*, Proceedings of the International School of Physics "Enrico Fermi," Course CXLVII, edited by R.J. Hemley and G.L. Chiarotti (IOS Press, Amsterdam, 2002), p. 151.
- [26] E.D. Maksimov and D.Yu. Savrasov, *Solid State Commun.* **119**, 569 (2001).
- [27] N.W. Ashcroft, in *Frontiers of High Pressure Research II: Application of High Pressure to Low Dimensional Novel Materials*, edited by H.D. Hochheimer *et al.* (Kluwer Academic Publishers, The Netherlands, 2001), p. 87. Ammonia and the metal amines are hydrogen rich as are, for example, B_2H_6 , YH_3 (Wijngaarden *et al.* [7]), and so on. One even notes that $\text{C}_2\text{H}_5\text{OH}$ is two-thirds hydrogen.
- [28] C.F. Richardson and N.W. Ashcroft, *Phys. Rev. B* **55**, 15 130 (1997).
- [29] H. Rosner, A. Kitaigorodsky, and W.E. Pickett, *Phys. Rev. Lett.* **88**, 127001 (2002).