Transient High-Temperature Superconductivity in Palladium Hydride

A Thesis submitted for the Degree of

Doctor of Philosophy

By

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Statement of Originality

This research work contains no material which has been submitted for a degree or diploma in any university, and to the best of my knowledge contains no material previously written or published by another person, except where due reference is made.

Syed Muhammad Hasnain
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This project was begun in May 2012, and in the intervening four years I have received constant support, encouragement and expertise from colleagues, family and friends. It would have been very difficult in the completion of this project, if not possible, without this assist and so I set about now to acknowledge them all.

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Abstract

Superconductivity in the palladium-hydrogen system has been studied experimentally by measuring the electrical resistivity. Loading a palladium sample to a stoichiometric ratio close to unity resulted in high-temperature superconductivity at \( \approx 55 \) K for PdH\(_x\) and \( \approx 60 \) K for PdD\(_x\). To observe the superconductivity it was necessary to cool the sample quickly from 300 °C and measure the resistivity while heating quickly.

For this project an important driver was a series of publications reporting the occurrence of superconductivity near room temperature with hydrogen-to-palladium ratio reaching 1. These results are still considered as controversial because they have not been reproduced. One of the other important driving factors was that PdH\(_x\) formed at about 300 °C exhibits different behaviour compared to the hydride formed by passage through the two-phase region at room temperature. This system does not form dislocations if the hydrogen absorption takes place above the thermodynamic critical point, which lies just below 300 °C.

In the 1970s, a superconducting transition temperature, \( T_c \), of about 9–10 K was reported for palladium hydride and 11–12 K for palladium deuteride. The new experiments performed in this project revealed that \( T_c \) has increased by a factor of about five by preparing the sample at high temperature.

Because the high-temperature superconductivity was transient, and at first not reproducible, a lot of work was done to first of all make the results more repeatable, by improving the thermal time response of the apparatus. This allowed the sample to be cooled and heated more quickly. The repeatability of the results improved and the
transition temperature increased slightly. Next, hydrogen was replaced by deuterium and an inverse isotope effect was observed, as could be expected by analogy with the low-temperature superconducting state. The disappearance of the superconducting state in a magnetic field provided further evidence that the observed phenomenon is real.

The occurrence of a significant isotope effect is strong evidence for BCS-type superconductivity. The question is how the state of the hydride formed at 300 °C differs from the usual state obtained at room temperature so as to increase $T_c$ so dramatically. A qualitative interpretation is proposed based on occupation of tetrahedral rather than octahedral interstitial sites in the Pd lattice. Work by others shows that the electronic energies of PdH$^{tet}$ and PdH$^{oct}$ at zero temperature are very similar and in fact if the H zero-point energy is ignored, PdH$^{tet}$ is significantly more stable, with an expanded lattice. Adding the zero-point energy reverses the order of stability. This suggests that some tetrahedral occupancy is possible at high temperatures and is frozen-in by rapid cooling. Calculations (by others) of the phonon spectrum and density of states for PdH$^{oct}$ and PdH$^{tet}$ show that the effect of tetrahedral occupancy on the optical branches is strong, with the introduction of very high frequency modes. These high-frequency modes may in fact contribute significantly to increasing the electron–phonon coupling, thus increasing $T_c$. Therefore it is proposed that tetrahedral occupancy is responsible for the observed high-temperature superconductivity.
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To my parents...
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Introduction

1.1 Motivation

Two factors motivated this project to search for high-temperature superconductivity in the palladium–hydrogen system. First were the papers by Tripodi et al. [1-3] reporting superconductivity near room temperature in samples with stoichiometry approaching PdH. No other group has reproduced their results. Second was the knowledge that PdH$_x$ formed at about 300 °C, and therefore having no dislocations, exhibits interestingly different behaviour (retains hydrogen for hours or days after forming Pd-D above the critical point (unpublished), even when the surroundings are evacuated; partial occupancy of tetrahedral interstices) compared to the hydride obtained by passage through the two-phase region at room temperature.

1.2 Superconductivity – Basic Properties

1.2.1 Superconductivity Phenomenon

In 1908 the liquefaction of helium gas opened a new field of low-temperature investigations of materials. In 1911 [4] Heike Kamerlingh Onnes discovered
superconductivity, evidenced by the electrical resistance of pure mercury totally disappearing below the critical temperature $T_c = 4.2$ K (Figure 1-1).

![Figure 1-1: (a) Vanishing resistance, (b) Meissner effect [5].](image)

Zero electrical resistance is the basic characteristic of a superconductor and gives superconductors their present and potential importance in technologies that are enhanced or made possible by lossless electrical conduction.

The Meissner effect [5] is the next most important property of a superconductor, whereby an ideal superconductor behaves like a perfect diamagnet, expelling all magnetic flux from its interior, as long as the applied magnetic field is small (Figure 1-1). The magnetic induction $\mathbf{B}$ is given by:

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M})$$  \hspace{1cm} (1.1)

where $\mathbf{H}$ is the applied magnetic field (magnetic intensity) and $\mathbf{M}$ is the magnetization. Complete flux expulsion implies $B = 0$ inside the superconductor, so

$$\chi \triangleq \frac{H}{M} = -1$$  \hspace{1cm} (1.2)
in this ideal case, where \( \chi \) is the (dimensionless) magnetic susceptibility. In general, \( \chi \) is negative in the superconducting state.

The third most important property of superconductors is the Josephson effect [5], in which a DC supercurrent tunnels between two superconducting blocks separated by a thin insulating barrier.

The origin of the metal-to-superconductor transition is electronic and involves a phase transition of second order with a discontinuity in the heat capacity at \( T_c \).

### 1.2.2 Types of superconductors

A superconductor can be basically classified as one of two types (Type I and Type II) depending on how its magnetization responds to an applied magnetic field. When \( H \) exceeds a critical value (\( H \geq H_c \)), superconductivity will be destroyed, even though \( T < T_c \). Type I superconductors transform directly to the normal (resistive) state, with \( H_c < 1 \) kOe, depending on the material. Type II superconductors enter a mixed (vortex) state from the perfect diamagnetic state at the lower critical field (\( H_{c1} \)) and finally enter the normal state at the upper critical field (\( H_{c2} \)), which may be many kOe. The corresponding phase diagrams are shown in Figure 1-2.
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Figure 1-2: Critical magnetic field as a function of temperature for (a) Type I superconductors, (b) Type II superconductors [6].

The state of a Type II superconductor below $H_{c1}$ is essentially the same as Type I, with $\chi = -1$. In the mixed state between $H_{c1}$ and $H_{c2}$, partial penetration of the magnetic field occurs. Normal regions conducting magnetic flux are surrounded by circulating supercurrents (vortices).

Most elemental superconductors are Type I, excepting V, Nb and Tc. Most superconducting alloys and compounds, including all families of HTS oxide superconductors, as well as a few metal hydrides are Type II. Type II materials are more useful for practical applications because superconductivity persists up to $H_{c2}$.

1.3 Applications

Superconductors have been successfully utilized in many practical applications, especially in superconducting magnets (solenoids). Superconductivity is an enabling technology for magnetic resonance imaging and possibly for very-high-speed maglev
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trains. Current and potential technological applications of superconductors are listed in Figure 1-3.

**Figure 1-3: Applications of superconducting materials.**

The technical and economic practicality of applications relying on superconductors is determined by $T_c$, $H_{c2}$ and the critical current, $J_c$, which generates a sufficiently high magnetic field to destroy the superconductivity. Values of $T_c$ above 78 K are especially important for large-scale installations, since liquid nitrogen can be used to maintain the operating temperature. The prospect of room-temperature superconductors is exciting because no cryogenic cooling would be required. Thus far,
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despite numerous reports, no instances of room-temperature superconductivity have been independently confirmed.

1.4 Theoretical Models

The superconductivity phenomenon has always been a very interesting but complicated problem for theoreticians. Early attempts at a theory were phenomenological. They described the observed superconductivity phenomena without giving any explanation of their microscopic origins. The first successful microscopic theory, based on the concept of phonon-mediated electron–electron interactions, was proposed in 1957 by Bardeen, Cooper and Schrieffer [7]. The BCS theory is able to account semi-quantitatively for both Type I and Type II superconductivity. High-temperature oxide superconductors are not understood via BCS theory.

1.4.1 Phenomenological models

These are not merely historical curiosities, because they introduced parameters that characterise Type I and Type II superconductors.

The London brothers derived a set of electrodynamic equations describing zero resistance and the Meissner effect [8]. According to this model there are two groups of electrons, the superconducting electrons present below the transition temperature $T_c$ and the normal electrons present above $T_c$. The London equations are

\begin{align}
\text{(CGS)} \quad \vec{j} &= \frac{c^2}{4\pi\lambda_L^2} \vec{E} ; \\
\text{(SI)} \quad \vec{j} &= \frac{1}{\mu_0\lambda_L^2} \vec{E} \quad (1.3)
\end{align}

Where,
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\[ \lambda_L = \sqrt{\frac{m c^2}{4\pi n e^2}}; \quad (\text{SI}) \quad \lambda_L = \sqrt{\frac{\varepsilon_0 mc^2}{ne^2}} \]  \hspace{1cm} (1.4)

\[ \nabla \times \mathbf{j} = -\frac{c}{4\pi \lambda_L^2} \mathbf{B}; \quad (\text{SI}) \quad \nabla \times \mathbf{j} = -\frac{1}{\mu_0 \lambda_L^2} \mathbf{B} \]  \hspace{1cm} (1.5)

Here \( \lambda_L \) is the London penetration depth, which is characteristic of a given superconductor and measures the exponential penetration of the shielding supercurrent.

The coherence length, \( \xi_o \), is another important parameter. It is the maximum length over which superconductivity is produced by the correlation (pairing) between electrons and is given by [9]

\[ \xi_o = \frac{2h
u_F}{\pi E_g} \]  \hspace{1cm} (1.6)

where \( \nu_F \) is the Fermi velocity and \( E_g \) is the energy gap at the Fermi surface. These electron pairs condense into the same energy level and act more like bosons. The energy gap exists as the pair of electrons has slightly lower energy which suppresses the kind of collisional interactions resulting in normal-state resistivity. The material exhibits zero resistivity for temperatures such that the band gap energy is greater than the thermal energy. These parameters allowed a distinction to be made between Type I (\( \lambda < \xi_o \)) and Type II (\( \lambda > \xi_o \)) superconductors.

Ginzburg-Landau theory [10] introduces a parameter \( k \):

\[ k = \frac{2\sqrt{2}eH_c \lambda^2}{\hbar} \]  \hspace{1cm} (1.7)

where \( k < \frac{1}{\sqrt{2}} \) for Type I and \( k > \frac{1}{\sqrt{2}} \) for Type II superconductors.
Scattering of fermionic conduction electrons by phonons, defects or impurities gives rise to the resistance of a metal in its normal state. The explanation of classic superconductivity in metals as the result of an electron–phonon interaction was first proposed by Abrikosov [11]. The origin of the attractive potential between electron pairs was explained in the microscopic theory of Bardeen, Cooper, and Schrieffer (BCS) [12]. In the BCS picture [7], the electron–phonon interaction can lead to electron–electron attraction close to the Fermi level and the condensation of boson-like Cooper pairs into the superconducting ground state. A dynamic deformation of the lattice (phonon) occurs as an electron passes through it, which results in a positive charge concentration in that region. This positively charged region then attracts another electron, forming a correlated Cooper pair (Figure 1-4). These two electrons have opposite spin (hence the boson-like behaviour) and momentum with a binding energy characteristic of the material. The electron–electron interaction can lead to a ground state which is separated from the excited state by an energy gap. Most of the electromagnetic properties, thermal properties, and the critical field are consequences of the energy gap. The coherence length and the penetration depth appear as real consequences of the BCS theory of superconductivity. The London equation is recovered for slowly varying (in space) magnetic fields. The fundamental phenomena of superconductivity — lossless conduction, the Meissner effect and the discontinuity in heat capacity — can be successfully explained within the BCS picture.
Figure 1-4: (a) Formation of Cooper pairs; a passing electron attracts the lattice, causing a slight ripple toward its path, another electron passing in the opposite direction is attracted to that displacement. (b) Electron-Phonon interaction; the behaviour of superconductors suggests that electron pairs are coupling over a range of hundreds of nanometers, three orders of magnitude larger than the lattice spacing. Called Cooper pairs, these coupled electrons can take the character of a boson and condense into the ground state [6].
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One of the requirements of this theory is that the screened Coulomb potential must be less than the electron–phonon potential, so that close to the Fermi surface there exists a net attractive potential. This phonon interaction between the two electron states $(\vec{k} \uparrow, -\vec{k} \downarrow)$ and $(\vec{k}' \uparrow, -\vec{k}' \downarrow)$ is given by [7, 13, 14]

$$V_{\text{phonon}} = \frac{2|M_q|\hbar \omega_q}{(\varepsilon_k - \varepsilon_{k'})^2 - (\hbar \omega_q)^2} \quad (1.8)$$

where $\vec{k} = \vec{k}' + \vec{q}$, $|M_q|$ is the matrix element of the electron–phonon interaction, $\hbar \omega_q$ is the energy of a phonon with wavevector $\vec{q}$ and $\varepsilon_k$ is the relative energy of an electron with wavevector $\vec{k}$. Given that the superconducting properties of many materials are similar, this interaction should not depend on the details of Eqn (1.8) [14] and can be approximated by

$$V_{\text{phonon}} = -V \to |\varepsilon_k|, |\varepsilon_{k'}| \leq \hbar \omega_q \leq \hbar \omega_D$$

$$= 0 \to \text{elsewhere} \quad (1.9)$$

where $(V)$ is constant and

$$\hbar \omega_D = k_B \theta_D \quad (1.10)$$

where $\theta_D$ is the Debye temperature corresponding to the Debye cut-off frequency $\omega_D$. The dependence of the transition temperature on the isotopic mass is a consequence of the Debye cut-off [14]. Thus

$$T_c \propto H_0 \propto \theta_D \propto (M_{\text{ION}})^{-1/2} \quad (1.11)$$

where $M_{\text{ION}}$ is the isotopic mass and $H_0$ is the critical magnetic field at absolute zero.
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For $T_c \ll \theta_D \text{ i.e.,}$, a weak interaction, this theory gives [7],

$$T_c \approx 1.14 \theta_D \exp \left( -\frac{1}{N(0)\lambda_{ee}} \right)$$  \hspace{1cm} (1.12)

where $\lambda_{ee}$ is the electron–phonon interaction potential and $N(0)$ is the electron density of states at the Fermi level. The transition temperature can only be increased if $\theta_D$ and/or the electron–phonon coupling constant $\lambda = N(0)\lambda_{ee}$ increases. Eqn (1.12) is fairly successful in predicting rough values for $T_c$, although calculating $\lambda$ from first principles is difficult [15, 16].

The penetration depth and coherence length, originally introduced via the phenomenological London and Ginzburg-Landau equations, emerge naturally in BCS theory [7].

The energy gap $E_g = 2\Delta$ is related to $T_c$ via

$$\Delta = 3.2 k_B T_c \sqrt{\frac{T_c - T}{T_c}}$$  \hspace{1cm} (1.13)

Explanation of the experimentally observed isotope effect ($T_c \propto \sqrt{M}$ where $M$ is the isotopic mass of the vibrating atom) is another important success of BCS theory, with particular relevance to the project reported in this Thesis.

1.4.3 Beyond the BCS theory of superconductivity

For $T_c \ll \theta_D \text{ i.e.,}$, the weak-coupling limit, BCS theory gives

$$T_c \approx 1.14 \theta_D \exp \left( -\frac{1}{N(0)\lambda_{ee}} \right)$$  \hspace{1cm} (1.14)
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The effective electron–electron interaction, $V_{ee}$, is composed of an attractive electron–phonon part, $V_{ep}$, and a repulsive Coulomb part, $V_C$:

$$N(0)V_{ee} = N(0)V_{ep} - N(0)V_C = \lambda_{BCS} - \mu$$

(1.15)

where $\lambda_{BCS} = N(0)V_{ep}$ is the electron–phonon coupling constant. The contribution from Coulomb repulsion, $\mu = N(0)V_C$ should be reduced (renormalised) to account for the much smaller retardation of the Coulomb screening relative to that of the electron–phonon interaction [17, 18]:

$$\mu^* = \frac{\mu}{1 + \mu \ln(\omega_p/\omega_D)}$$

(1.16)

where $\omega_D$ is the Debye frequency and $\omega_D$ is the plasma frequency. $1/\omega_D$ and $1/\omega_p$ represent the propagation times of the electron–phonon attraction and the screened Coulomb repulsion, respectively. $\mu^*$ is referred to as the Coulomb pseudopotential. Then

$$N(0)V_{ee} = \lambda_{BCS} - \mu^*$$

(1.17)

In 1968 McMillan [19] extended the BCS picture to account for strongly coupled superconductors, for which he proposed

$$T_c \approx \frac{\omega_D}{1.45} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right]$$

(1.18)

In Eqn (1.18) $\lambda$ plays the same role as $\lambda_{BCS}$ in Eqn (1.17) and is defined in terms of the Eliashberg spectral function $\alpha^2(\omega)F(\omega)$ [17-19]:

$$\lambda = 2\int_0^\infty \frac{1}{\omega} \alpha^2(\omega)F(\omega)d\omega$$

(1.19)
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where

\[ a^2(\omega) F(\omega) = \frac{\int_{FS} \frac{d^2k}{v_F} \int_{FS} \frac{d^2k}{v_F} \sum_{\nu} \left| g(k,k',\nu) \right|^2 \delta(\omega - \omega_H(q,\nu))}{\int_{FS} \frac{d^2k}{v_F}} } \tag{1.20} \]

The integrals are performed over the Fermi surface and we recognise that

\[ N(0) = \frac{V}{(2\pi)^3 h^3} \int_{FS} \frac{d^2k}{v_F} \tag{1.21} \]

In Eqn (1.20) \( g(k,k',\nu) \) is the matrix element corresponding to the scattering of an electron in state \( |k\rangle \) (at the Fermi surface) to state \( |k'\rangle \) by a phonon with wavevector \( q \) and polarisation \( \nu \):

\[ \left| g(k,k',\nu) \right|^2 = \frac{1}{2MNt \omega(q,\nu)} I^2(\nu) \tag{1.22} \]

where \( q = k' - k - g \). \( g \) is a reciprocal lattice vector and \( g \neq 0 \) corresponds to Umklapp processes as usual. In Eqn (1.22) \( I(\nu) \) is the electronic matrix element corresponding to the change in the crystal potential, \( U \), as one atom is moved:

\[ I(\nu) = \langle k | \mathbf{e}(q,\nu) \cdot \nabla U | k' \rangle \tag{1.23} \]

where \( \mathbf{e}(q,\nu) \) is the polarisation vector of the phonon.

The general moment of \( a^2(\omega) F(\omega) \) is defined by

\[ \left\langle \omega^n \right\rangle \triangleq \frac{2}{\lambda} \int_0^\infty \omega^{n-1} a^2(\omega) F(\omega) d\omega \tag{1.24} \]
where \((2/λ)\omega^{-1} \alpha^2(ω) F(ω)\) is the weighting function on \(ω^n\).

Following McMillan [19], calculating the first moment of \(\alpha^2(ω) F(ω)\) gives

\[
\frac{\lambda}{2} \langle ω^2 \rangle = \int_0^\infty ω \alpha^2(ω) F(ω) dω = \frac{\int_{FS} dS \int_{FS'} dS' \frac{dS}{(2\pi)^3 v_F} \sum_{\nu} \frac{1}{2MN} l^2_v(k,k',\nu)}{\int_{FS} dS' v_F} \tag{1.25}
\]

\[
= \frac{N(0)\langle I^2 \rangle}{2M}
\]

giving for the electron–phonon coupling constant

\[
\lambda = \frac{N(0)\langle I^2 \rangle}{M \langle \omega^2 \rangle} = \frac{η}{M \langle \omega^2 \rangle} \tag{1.26}
\]

where \(\langle I^2 \rangle\) is the mean-square electronic matrix element, \(M\) is the ionic mass and \(\langle \omega^2 \rangle\) is the (weighted) mean-square phonon frequency. Eqn (1.26) has been the basis for connecting theory and experiment. Its importance lies in the separation of the purely electronic contributions \((η)\) in the numerator from the phonon contributions in the denominator.

After some simplifying assumptions, a theoretical maximum value for the transition temperature was derived by McMillan:

\[
T_c^\text{max} \approx \left(\frac{C}{2M}\right)^{3/2} e^{-3/2} \tag{1.27}
\]

where \(C\) is a constant for each class of materials. In this model \(T_c\) attains its maximum value for \(λ = 2\) and is much less than \(T_c^\text{max}\) for \(λ < 1\). The values of \(T_c^\text{max}\) calculated for the then known metallic superconductors with the highest measured values of \(T_c\) were 28 K and 40 K for Nb₃Sn and V₃Si respectively. These findings led to the still-common
statement that the upper limit for BCS superconductivity is 30–40 K. The upper limit \( \lambda = 2 \) was shown to be spurious by Allen and Dynes [16]; there is no universal upper limit to \( T_c \), a significant point in relation to this work.

The prefactor in McMillan’s equation only applies to materials with phonon density of states (PDOS) similar to that of niobium. A subsequent refinement of the model by Allen and Dynes [16] led to a more widely applicable formula:

\[
T_c = \frac{f_1 f_2 \omega_{\log}}{1.2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62 \lambda)} \right] \tag{1.28}
\]

where

\[
\ln \left( \omega_{\log} \right) = \int_0^\infty \frac{\ln(\omega)}{\omega} \alpha^2(\omega) F(\omega) d\omega \left/ \int_0^\infty \frac{1}{\omega} \alpha^2(\omega) F(\omega) d\omega \right. \tag{1.29}
\]

and \( f_1 f_2 \approx 1.03 \) [20] and can be ignored.

McMillan’s theory strictly applies to an elemental superconductor and requires modification to deal with the very different masses of H/D and Pd. Papaconstantopoulos, et al. [21] showed that this extension may be accomplished by summing the contributions from (in this case) Pd and H/D:

\[
\lambda = \sum_j \lambda_j \quad (j = \text{Pd or H/D}) \tag{1.30}
\]

\[
\lambda_j = \frac{\eta_j}{M_j \langle \omega_j^2 \rangle} \tag{1.31}
\]

where the mean-square frequency contributions relate the site-decomposed contributions to the phonon density of states in Eqn (1.24). Because the mass of Pd is so
much greater than those of the hydrogen isotopes, \( F_{Pd}(\omega) \) is dominated by the acoustic part of the total phonon spectrum whereas \( F_{H/D}(\omega) \) is dominated by the optical part.

A further refinement occurs by recognising that the electronic structure is affected by the high-amplitude zero-point motion of H/D. This is conveniently done by incorporating a Debye-Waller factor into the electronic component of \( \lambda \) [20, 22, 23]:

\[
\eta_{H/D} = \eta_{H/D}^0 e^{-2W} \tag{1.32}
\]

To account for the effect of the motion of the Pd atoms on the vibration of the H/D atoms, Yussouff, et al. [20] write the Debye-Waller factor as

\[
2W = \frac{12\pi^2\hbar^2}{a^2Mk_B\theta_D} \tag{1.33}
\]

where \( \theta_D \) is a re-defined effective Debye temperature related to the entire phonon spectrum (via \( \omega_{log} \)), not just the optical part:

\[
\theta_D = \frac{1.45 f_1 f_2 \omega_{log}}{1.20} \tag{1.34}
\]

The final element of a successful theory of strongly-coupled superconductivity in Pd–H2/D2 is to incorporate an anharmonic potential into the rigid-ion calculation of the \( \langle I^2 \rangle \) factor in \( \eta_{H/D}^0 \) (Eqn (1.32)), without which the reverse isotope effect between H and D cannot be modelled. With these refinements, a fairly successful calculation of \( T_c \) can be made for PdH, PdD and PdT [20, 24, 25]. Within the formalism developed by Yussouff, et al. [20], Eqn (1.33) is used to calculate the Debye-Waller factor to be applied to \( \eta \) and then the Allen-Dynes equations (Eqns (1.28) and (1.29)) are used to calculate \( T_c \).
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Allen and Dynes [16] conclude that to increase $\lambda$ it is more important to increase $\eta$ than to decrease $\langle \omega^2 \rangle$. Lowering $\langle \omega^2 \rangle$ owing to soft phonon modes, say, does increase $\lambda$, but it also decreases $\omega_{\text{log}}$ in Eqn (1.28).

1.4.4 Other theories

While the BCS theory successfully explains the principal features of conventional superconductors, it does not explain the mechanism of high temperature superconductivity in oxide or pnictide superconductors. These theories are briefly mentioned for completeness, but the BCS picture appears to be most relevant to this project.

The Resonance Valence Band (RVB) model developed in by Anderson in 1973 [26] is one of the leading theories now proposed to explain high-temperature superconductivity. In place of Cooper pairs, a condensate consisting of holon pairs is formed. This quasiparticle is essentially an empty site along with the rest of the singlet-bonded electrons and resonates in a coherent way among different valence bond configurations.

Other pictures of high-temperature superconductivity include the spin-bag mechanism [27], which describes the pairing of two holes such that the interaction between them overpowers their Coulomb repulsion, mechanisms involving excitons and plasmons [28, 29], Ginzburg's proposal [30] that the electron–phonon interaction is responsible and Mott's picture [31] resembling bipolaron theory.
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1.5 Hydrogen in superconductors

Three reasons can be advanced to study the effects of hydrogen absorption by superconductors. First, hydrogen absorption generally causes lattice expansion and so, roughly speaking, the opposite effect to compression by hydrostatic pressure. This provides an additional and valuable way to probe the dependence of superconductivity on lattice structure, electronic structure and the phonon spectrum. Secondly, hydrogen absorption carries the prospect of enhanced critical superconducting properties such as critical temperature $T_c$, critical current density $j_c$, and critical fields ($H_{c1}, H_{c2}$), although it must be acknowledged that no technologically worthwhile enhancement has so far been confirmed. On the other hand, the present record for $T_c$, established very recently [32] is 203 K, for a hydrogen-containing superconductor, H$_2$S under high hydrostatic pressure. Thirdly, compatibility with hydrogen and its isotopes is a potentially significant factor for applications such as superconducting electric power transmission cables and fusion reactors, where exposure of superconducting components to hydrogen may lead to absorption despite protective cladding.

Superconductivity in hydrogen-containing materials was initially a surprising conjunction of notionally disparate fields: conventional metallic superconductivity and metal hydrides. On the other hand, given that the absorption of a proton, typically into an interstitial site in the metal lattice and an electron, into the band structure, usually significantly affects the crystal structure, band structure, phonon spectrum and therefore all physical properties of many metals, alloys and intermetallics, it is surprising that few metallic superconductors in which hydrogen plays a role are well known. In either case, superconductors created or altered (for better or worse) by uptake of hydrogen have great potential to improve our understanding of superconductivity.
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Even at low concentrations, an interstitial solution of H in metal results in distortion of the surrounding lattice and influences physical properties. Atypical behaviours of the lattice parameters, elastic constants and thermoelectric power of notionally pure metals have been explained as consequences of low concentrations of hydrogen as an impurity [33].

1.6 Palladium hydride

Palladium hydride (PdHₓ, where \( x \approx 0.6 \) at room temperature) was reported by Graham in 1866 [34] and is the best-known metal hydride (where "hydride" is taken to include non-stoichiometric compositions MHₓ for any value \( x > 0 \)). Palladium absorbs hydrogen readily from H₂ gas at less than 1 atm pressure at room temperature. This happens by the hydrogen molecule first being weakly attracted to the palladium surface, followed by dissociation of the molecule to two H atoms that are more strongly bound, followed by the H atom diffusing into the metal via interstices in the metal crystal lattice and occupying these interstices up to a hydrogen-to-metal atomic ratio (H/M or \( x \) in MHₓ), approaching one at high pressure and low temperature [35]. As the hydrogen pressure over the metal increases, the dilute solid-solution phase (\( \alpha \)) becomes unstable and the concentrated hydride phase (\( \beta \)) forms. Ordering of hydrogen in the \( \beta \) phase occurs at cryogenic temperatures. Kilobar H₂ pressures are required to achieve \( x = 1 \) by reaction with hydrogen gas near room temperature [35, 36].

Whereas Pd metal is an enhanced Pauli paramagnet owing to the high density of states at the Fermi level, addition of H progressively fills the 0.6-electron hole in the \( d \) band, so that for \( x > 0.6 \) at room temperature the hydride is diamagnetic [37]. Adding electrons into the \( s \) band from further H absorption occurs at a higher energy per electron, causing the necessary H₂ gas pressure to rise rapidly.
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At room temperature and below, $H$ occupies octahedral interstices ((a) in Figure 1-5), forming a sodium-chloride structure. At temperatures above about 300 °C it appears that some hydrogen occupies tetrahedral interstices ((b) in Figure 1-5) [38]. This is a key point for the work reported here.

Figure 1-5: Schematic atomic structure of stoichiometric palladium hydrides, with $H$ occupying (a) octahedral (o-Pd-H) and (b) tetrahedral (t-Pd-H) interstitial sites.

1.7 Palladium hydride as a superconductor

Palladium hydride, $\text{PdH}_x$ where $0.7 < x < 1.0$, is also the best-known superconducting hydride, first reported by Skoskiewicz in 1972 [39], with $T_c = 9–10$ K for $x \approx 1.0$ [40-46]. This will be referred to as low-$T_c$ superconductivity. Within the BCS picture, the influence of hydrogen can be understood qualitatively as arising in coupling of optical phonons to the electron system, leading to the expectation of an isotope effect in which heavier interstitials lower $T_c$. Palladium deuteride, $\text{PdD}_x$, exhibits a reverse isotope effect [40, 46], with $T_c = 11–12$ K for $x \approx 1.0$. This discovery
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generated great interest and controversy by apparently contradicting the predictions of simple BCS theory. Nevertheless, the superconducting properties of low-$T_c$ PdH$_x$ /PdD$_x$ can be understood within the BCS picture, despite the reverse isotope effect, which is mainly a consequence of anharmonicity of the interatomic potential seen by H/D [47]

1.8 Thesis Structure

Chapter 1, “Introduction”, introduces the motivations of the project and the context of the thesis. Some important concepts and background are explained which are necessary to follow the more detailed discourse in the later chapters.

Chapter 2, “Literature review”, gives a summary of the existing literature appropriate to this subject and also features some of the trends in current and future research.

Chapter 3, “Materials and Methods”, gives details about the materials and experimental techniques.

Chapter 4, “Discovery of High-Temperature Superconductivity in the Palladium-Hydrogen (Deuterium) System”, summarises the resistivity measurements on PdH$_x$ /PdD$_x$ that demonstrate the occurrence of high-temperature superconductivity with a reverse isotope effect.

Chapter 5, “Discussion and Interpretation of Experimental Results”, details the discussion on the important findings of previous chapter, with a possible explanation of high-temperature superconductivity in PdH$_x$ /PdD$_x$.

Chapter 6, “Conclusions and Perspectives”, gives a summary of the whole work and the most important findings, with suggestions for future research on this topic.
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### Chapter 2. Literature Review

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2.1 Historical Background

The first investigation of superconducting metal hydrides appears to be that of Horn and Ziegler [1], as early as 1947. Hydrides of tantalum and niobium were found to have depressed values of $T_c$ compared to the pure metals.

Superconductivity enhanced by interstitial hydrogen was first reported in 1970 in the thorium–$H_2$ system, Satterthwaite and Toepke [2] found Th$_4$H$_{15}$ to be superconducting below about 8 K, compared to $T_c = 1.37$ K for pure thorium.

In the light of predictions that metallic hydrogen is a superconductor with transition temperature possibly above 100 K [3-6], the ability of Pd to take up hydrogen at high number density ($6 \times 10^{28}$ m$^{-3}$ at 1 H per Pd) led to speculation that metallic hydrogen might be responsible for the superconductivity of PdH$_x$ [7]. This speculation inspired a number of theories and experiments during the 1970s. However, the consistent indication from experiments is that metallic hydrogen is not responsible for superconductivity in PdH$_x$ [7].

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investigation of the high-\(T_c\) cuprate superconductor \(\text{YB}_2\text{Cu}_3\text{O}_7\) [14], superconducting hydrides attracted relatively little further experimental attention until the discovery of superconductivity in \(\text{MgB}_2\) [15, 16], with \(T_c \approx 38\) K, and the report of increased \(j_c\) at high fields owing to implantation of protons [17]. Only a small increase in \(T_c\) accompanied the effective uptake of H. Subsequently, Ashcroft [18] argued that the dense group 14 hydrides such as \(\text{SnH}_m\) [19] might exhibit high-temperature superconductivity at pressures considerably lower than required to form metallic hydrogen.

Tripodi et al. [20, 21] claim to have repeatedly observed superconductivity in electrolytically loaded \(\text{PdH}_x\) at much higher temperatures than previously, almost up to room temperature. Lipson et al. [22, 23] have reported anomalies in the electrical and magnetic properties of \(\text{PdH}_x\) at temperatures up to nearly 70 K that were interpreted as indicating filamentary superconductivity.

In this chapter the known hydrogen-containing superconductors are surveyed, including H-modified metallic, cuprate, pnictide and carbon-based superconductors. The aim was to review materials rather than explanations of superconductivity.

2.2 Hydrides and superconductors in the periodic table

Many elements that form metal hydrides are also superconductors, although few superconducting hydrides have been found. One practical reason might be that when an element or alloy is exposed to hydrogen atmosphere under certain temperature and pressure conditions, the hydrogenated material in that new state may not be stable once the thermodynamic driving forces are removed.
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2.2.1 Hydrides

Figure 2-1 shows a periodic table of binary elemental hydrides [24], indicating the nature of the hydrides. The reaction of hydrogen with Groups 1–2 alkali and alkaline-earth metals generally forms ionic hydrides, although BeH$_2$ and MgH$_2$ have a bonding character intermediate between ionic and covalent. These hydrides are typically semiconducting (see ref. [25] for a recent survey).
Figure 2-1: Periodic table of elemental hydrides (after [24]).
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Hydrogen reacts exothermically with transition metals in Groups 3–5 to form metallic, semi-metallic and semi-conducting hydrides. These hydrides generally form readily at modest hydrogen pressures, although elevated temperatures are sometimes required.

Previously hydrogen was considered not to form stable hydrides of the transition metals in Groups 6–10 under normal conditions of temperature and hydrogen pressure, with Pd a notable exception (see the "hydride gap" in Figure 2-1). The "hydride gap" was largely filled-in by 2000, following progress in the technology of compressing gaseous hydrogen to gigapascal pressures. The field was reviewed by Antonov [26] and many metals are now known to form hydrides at elevated pressures. For instance, while Ni dissolves only a very small amount of hydrogen under normal conditions, it forms an interstitial hydride at 3.4 kbar at 300 K [27]. These hydrides have close-packed metal sublattices with fcc, hcp or dhcp structure [28], in which hydrogen occupies octahedral interstitial positions [29-31].

The interstitial hydrides absorb hydrogen atoms (p+e⁻) by the hydrogen molecule first being weakly attracted to the metal surface (physisorption), followed by dissociation of the molecule into two H atoms that are more strongly bound (chemisorbed), followed by the protons diffusing into the metal via interstices in the metal crystal lattice and occupying these interstices, while the electron is incorporated into the electronic structure. Absorption up to a hydrogen-to-metal atomic ratio, H/M, that may exceed one (e.g. TiH₂) and number densities exceeding those of liquid and solid H₂ are common [32].

Of the Group 11 metals, only Cu is known to form a hydride. This hydride phase can be observed at pressure higher than 14.4 GPa and it retains fcc crystal structure of
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copper where hydrogen atoms occupy interstitial sites at hydrogen to metal atomic ratio of \( \sim 0.4 \) [33]. The volatile metals (Group 12) form intermediate hydrides.

Of the Group 13 metals, Al forms a hydride (alane, AlH\(_3\)) under very high hydrogen pressure [34]. B and Ga are also capable of forming many compounds with hydrogen and the rest of the group is not known for forming stable hydrides. The Group 14–17 elements form covalent hydrides.

Concentrated interstitial alloys of hydrogen in metals have been studied and developed intensively since the 1970s because of their potential for storing hydrogen fuel [1]. This class of metals includes many \( d \) metals, famously Pd, and intermetallics, especially AB\(_5\) (archetype LaNi\(_5\)) and AB\(_2\) (archetype TiCr\(_2\)) compositions. In all these cases the metallic nature of the host metal is preserved in the hydride. While the A element is generally regarded as hydride forming, (e.g. LaH\(_3\), TiH\(_2\)), and the B element as non-hydride forming, in reality interstitial hydrides of B elements are formed under high hydrogen pressures, for example NiH [27].

The so-called complex hydrides, including MgH\(_2\), NaAlH\(_4\) and other "alanates", and the borohydrides such as Mg(BH\(_4\))\(_2\) also form from reaction of a metal with gaseous hydrogen under widely varying conditions that often involve high temperature or high pressure, or both. In these hydrides H occupies lattice sites and the formation of the hydride involves a change in crystal structure. Mg(BH\(_4\))\(_2\) is interesting in the context of this discussion because it forms from the high-temperature superconductor MgB\(_2\) [35, 36], with a transition temperature known to be increased by absorption of a small concentration of H atoms [17].

Rare earth hydrides can be formed easily at high temperature (600–800 °C) when the metal is exposed to a hydrogen atmosphere [37]. These hydrides represent a
fascinating group of interstitial compounds because of their electronic properties. One of the interesting characteristics is that the hydride phases formed can exist over significant composition ranges, encompassing, for example, di-hydrides (RH$_2$), and tri-hydrides (RH$_3$). In di-hydrides hydrogen atoms occupy nominally tetrahedral sites exhibiting the CaF$_2$-type structure, while the octahedral sites are occupied by tri-hydrides of the rare earth elements exhibiting BiF$_3$ type crystal structure. While the di-hydrides exhibit high electrical and thermal conductivities, with a metallic lustre, the tri-hydrides may be transparent. These properties are embodied in the reversible "switchable mirror" function of, for example, YH$_{2+3}$ [38], in which the optical transition follows introduction or removal of hydrogen gas.

2.2.2 Superconductors

As detailed in §2.4, superconductivity arises through an attractive interaction between electrons, leading to an energy gap at the Fermi energy and superconductivity of the cooperative ground state. The other universal features are the existence of a penetration depth, a coherence length and flux exclusion.

There are perhaps four distinguishable classes of superconductors corresponding to four different mechanisms for superconductivity [5]. The first group contains the s–p electron metals which are the metals in groups 2 through 16 of the periodic table (Figure 2-2) [39]. These are the earliest known superconductors and are also called “soft” superconductors. This is the only group among superconducting elements where an electron–phonon interaction is the known cause for the phenomenon of superconductivity.
Figure 2-2: Periodic table of elemental superconductors (after [39]).
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The second group includes the transition elements or the s–d electron elements. This class also includes compounds of the transition metals as well as compounds with s–p metals. In this class the maximum transition temperature is found for numbers of valence electrons close to 5 and 7 per atom (even numbers are expected to correspond to filled bands and low \( N(0) \)).

The third class of superconductors involves the non-magnetic and cubic metal compounds with high Debye temperatures, including compounds of the transition metals with light elements, particularly beryllides, nitrides, carbides and borides.

The superconductors that fall in the fourth and last class consist of the elements with a partially filled f shell, such as lanthanides.

2.3 **Experimental techniques for loading hydrogen**

Techniques for loading hydrogen into materials and measuring the uptake have been well established by the community working on hydrogen storage materials. The three principal techniques applied to H-modified superconductors, including ion implantation, are briefly described here. A common problem is that the hydrogenated state may not be stable once the thermodynamic driving force (gas pressure or electrochemical potential) for hydrogenation is removed. Hence the possibility of in-situ measurements of resistivity and/or magnetic susceptibility during hydrogenation is a crucial matter for exploring the influence of hydrogenation on superconductivity. The alternative is to stabilise the hydride against desorption by chemical treatment, which may interfere with the intrinsic characteristics of the material under study.
2.3.1 Absorption from the gas phase

2.3.1.1 Sieverts technique

This is the most commonly used technique used to measure hydrogen uptake by materials owing to its generally good accuracy, robustness and convenience.

The principle is that a known pressure of hydrogen is prepared in a calibrated reference volume then admitted to the sample chamber, stepwise. From measurements of the pressure in the reference volume before and after sharing hydrogen with the sample chamber via a connecting valve, the number of moles of H taken up in the \( k \)th step may be calculated as [40].

\[
\Delta n_H^k = 2 \left[ \frac{p_{\text{ref}}^k}{Z \left( \frac{p_{\text{ref}}^k}{T_{\text{ref}}} \right) R T_{\text{ref}}^k} - \frac{p_{\text{sys}}^k}{Z \left( \frac{p_{\text{sys}}^k}{T_{\text{ref}}} \right) R T_{\text{ref}}^k} \right] V_{\text{ref}}
- \left[ \frac{p_{\text{sys}}^k}{Z \left( \frac{p_{\text{sys}}^k}{T_{\text{cell}}} \right) R T_{\text{cell}}^k} - \frac{p_{\text{sys}}^{k-1}}{Z \left( \frac{p_{\text{sys}}^{k-1}}{T_{\text{cell}}} \right) R T_{\text{cell}}^{k-1}} \right] (V_{\text{cell}} - V_X)
\]

(2.1)

where "ref" refers to conditions in the reference volume, "cell" to conditions in the sample cell and "sys" to the pressure in the entire system after the connecting valve is opened. \( Z \) is the hydrogen compressibility and \( V_X = m_X / \rho_X \) is the volume occupied by the sample. Note that the mass of the sample, \( m_X \), and its density, \( \rho_X \), depend in general on its hydrogen content. The total change after \( N \) steps is

\[
n_H^N = \sum_{k=1}^{N} \Delta n_H^k
\]

(2.2)

The Sieverts technique is fundamentally prone to error because (i) the amount of H taken up in each step is calculated from the typically small difference between the two typically large terms in brackets in Eqn (2.1) and (2.2) the error per step accumulates. A detailed analysis is given in [41]. At high pressures, the amount of
hydrogen in the system may become large compared to the amount taken up by the sample, necessitating extra care to obtain accurate measurements. Nevertheless, by using a high-accuracy pressure transducer (0.01%) and carefully controlling and measuring temperature, the Sieverts technique may be applied accurately up to kbar gas pressures in a very wide range of temperatures, subject to the availability of accurate compressibility data.

The Sieverts technique is the approach most directly compatible with in-situ measurements of transport properties, since the sample can be maintained under hydrogen pressure while remaining accessible for electrical measurements via feed-throughs. Magnetic measurements are less easily accommodated at high pressure, but alternating susceptibility can be measured via a coil system internal to the sample cell, or external to it if the intervening cell material is relatively non-magnetic and not a good conductor.

2.3.1.2 Gravimetric technique

Even relatively small amounts of hydrogen uptake may be measured by weighing the sample in a sensitive balance. Microbalances with pressure ratings to hundreds of bar and a wide range of sample temperatures are available, although much more expensive than a basic Sieverts system. For the most general case of a beam balance with tare weight and sample suspended in the same working gas at different temperatures, the resultant balance force is
\[
\frac{F}{g} = m_s - m_t - \frac{M_p}{R} \left( \frac{V_s(T_s, p)}{Z(T_s, p)T_s} - \frac{V_t(T_t)}{Z(T_t, p)T_t} \right) + \Delta m_b - \frac{M_p}{R} \left( \frac{V_{bs}(T_s)}{Z(T_s, p)T_s} - \frac{V_{bt}(T_t)}{Z(T_t, p)T_t} \right) + \Delta m_h - \frac{M_p}{R} \left( \frac{V_{hs}(T_{hs})}{Z(T_{hs}, p)\bar{T}_{hs}} - \frac{V_{ht}(T_{ht})}{Z(T_{ht}, p)\bar{T}_{ht}} \right) + \Delta m_0 - \frac{M_p}{RZ(T_0, p)T_0} \Delta V_0.
\]

(2.3)

where \(m_s\) and \(m_t\) are the masses of the sample and the tare weight, \(M\) is the formula weight of the working gas, \(V_s\) is the volume of the sample that is not accessible to the working gas, \(V_t\) is the volume of the tare weight, which is assumed to be impervious to hydrogen, \(V_{bs}\) and \(V_{bt}\) are the volumes of the buckets (if any) on the sample and tare sides of the balance, \(\Delta m_b\) is the difference in the masses of the buckets, \(V_{hs}\) and \(V_{ht}\) are the volumes of the hangdown (suspension) components, \(\Delta m_h\) is the difference in the masses of the hangdown components on the sample and tare sides, \(\bar{T}_{hs}\) and \(\bar{T}_{ht}\) are effective temperatures for the hangdown components, which typically traverse zones in a range of temperatures between \(T_s\) and \(T_0\), the temperature at the balance beam, \(\Delta V_0\) is the difference in the effective volumes of the two sides of the balance beam and \(\Delta m_0\) is the difference in the effective masses of the two sides of the balance beam.

The gravimetric technique is prone to error arising in the buoyancy forces on the sample and tare weight owing to their immersion in the surrounding gas. This problem is formally identical to that of knowing the volume, \(V_X\), of the sample in the Sieverts technique [41, 42]. The gravimetric technique is generally more accurate than the Sieverts technique [42] but is much less capable of implementation for high hydrogen pressures.
On the other hand, while the gravimetric technique is generally unsuitable for electrical measurements because of the suspension of the sample, simultaneous measurements of the uptake of hydrogen and the magnetic moment of the sample are possible using the Faraday technique [43], in which a set of solenoids outside the sample chamber produces a magnetic field and field gradient. The magnetisation of the sample can then be calculated from the change in measured mass, $\Delta m_H$, due to the applied field and field gradient via

$$\frac{M}{H_0} = \frac{\Delta m_H g}{\mu_0 H_0 G_0}$$

(2.4)

where $H_0$ and $G_0$ are values respectively of the applied field and the gradient at the centre of the sample [43]. By making measurements with the gradient field in forward and reverse directions, both the amount of hydrogen taken up by the sample and its magnetisation may be calculated by taking sums and differences.

2.3.1.3 Other gas-loading techniques

While the Sieverts and gravimetric techniques have the advantage of simultaneous measurement of the amount of hydrogen in the sample, their use is restricted by the need for accurate data for the density (compressibility) of $H_2$ and $D_2$ [44]. Reliable density data are not available for temperatures below about 100 K, and are subject to dispute at pressures above several kbar [45, 46]. Thus, experiments in which H(D) is loaded at kbar pressures and above must rely on other techniques for estimation of the amount of H(D) in the sample [47, 48].

Buckel, et al. [47] charged Pd samples electrolytically before exerting pressure up to 21.6 kbar in a pressure cell. Schirber [48] loaded Pd with H(D) from the gas phase and applied He pressure up to 4(7) kbar. The hydrogen pressure was measured with a
manometer at room temperature during a careful isobaric cooling to 4 K. Hemmes, et al. [49] synthesised metal hydrides under pressures up to about 40 kbar H2 and D2 in a diamond-anvil cell (DAC). The DAC was first filled with liquid hydrogen, cooled to 20 K to condense hydrogen between the diamonds, then compressed to seal the hydrogen in, and finally heated to a temperature sufficient for H(D) diffusion into the sample, at which point the hydrogen pressure was ~ 35 kbar.

2.3.2 Electrochemical loading

Electrochemical loading of hydrogen at room temperature may achieve H contents that would require impractical H2 pressures at non-ambient temperatures for the same loading from the gas phase. This is readily understood by regarding the reaction as equilibrium between H in the electrochemical or gas phase and H in the solid phase. Whereas the free energy per H in the gas phase varies as the logarithm of gas pressure (\(\Delta G = 1/2 RT \ln \left( \frac{p}{p_0} \right)\)) per mole H, assuming ideal-gas behaviour), therefore increasing slowly at high pressure, that in the electrochemical phase is directly proportional to the potential difference acting on the H species in solution (\(\Delta G = FE\)) per mole of transferred charge). If no gaseous H2 is produced, the amount of H loaded into the cathode (moles of H) is just the amount of charge transferred. Evolution of an unknown amount of H2 necessitates measurement of the amount of H in the sample by an independent method, a disadvantage compared to loading from the gas phase.

Skoskiewicz [50] loaded hydrogen into Pd and Pd (Ni) alloys by electrolysis of 0.1-M H2SO4 at current densities of 50–150 mA/cm², with Pt leads spot-welded to the sample. The amount of hydrogen in the sample was controlled and measured by desorbing to a mass spectrometer.
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For ex-situ measurements of superconducting properties at cryogenic temperatures, stabilisation of the loaded hydrogen is required. Rapid cooling of the sample to a temperature low enough to inhibit H transport may suffice, but in the case of Pd a significant amount of hydrogen is likely to escape during cooling; even at 50–75 K, deuterium is mobile in PdDₓ on a time scale of many hours [51], although diffusion appears to slow at high D concentration.

An approach that partly overcomes this problem was used to prepare high-concentration hydrides by electrolysis [1]. Electrolysis was performed in HCl/methanol at –80 °C for times ranging from minutes to hours, after which the sample was submerged in liquid nitrogen to retain the hydrogen. We discuss this approach in §2.4.1.5.

Tripodi, et al. [21] stabilised highly loaded PdHₓ samples electrochemically, by the addition of Hg₂SO₄ to the electrolyte, thus coating the surface of the palladium hydride with a Pd–Hg amalgam layer some hundreds of nm thick. This layer, being impervious to diffusion of H, prevents migration to the surface and loss by recombination.

2.3.3 Ion implantation

Direct implantation of H⁺ (protons) and D⁺ was introduced by Stritzker and Buckel [52] as a means by which superconducting PdHₓ with x ≈ 1 could be made.

Implantation was carried out at 4 K to stabilise the implanted hydrogen. The average penetration depth of the H ions was about 1 μm at the H₂⁺ beam energy of 130 keV, resulting in a surface layer with a high concentration of implanted H some hundreds of nm thick on Pd foil. The foil was pre-charged with H (or D) by first heating
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to 300 °C under about 4 bar H₂ pressure to shorten the implantation time. An atomic ratio H/Pd of 0.7 was achieved, measured by weighing. Reference to the pressure–composition phase diagram for the Pd–H₂ system [53] makes it clear that while the sample was cooling under hydrogen pressure to room temperature it traversed the two-phase region. The foil was then quickly cooled to 77 K to minimise the loss of hydrogen prior to implantation. Ion implantation produces a very inhomogeneous hydrogen distribution which is frozen in by sufficiently low temperature. Inhomogeneity appears to be the cause of the broad superconducting transitions observed by Stritzker and Buckel [52]. In contrast, Schirber and Northrup [54] observed the sharpest transitions by charging Pd powder under 5 kbar H₂(D₂) and then lowering the temperature very slowly to achieve a homogeneous distribution of H(D) at a concentration of 0.99(0.97).

Ion implantation is accompanied by damage as the kinetic energy of the ion is dissipated in collisions, typically causing atomic displacements resulting in interstitials and vacancies and, if the vacancies coalesce, voids. This approach, with protons of 0.4–2.0 MeV, was used to induce damage in MgB₂ [17] that resulted in an increased high-field critical current density. The authors did not consider the effects of the residual implanted H species.

2.4 Hydrogen in superconductors

The long-held view that metal hydrides are non-superconducting and that superconductivity decreases as the concentration of hydrogen in the metal increases, beginning with Horn and Ziegler [1], was overturned when Satterthwaite and Toepke [2] and Skoskiewicz [50] discovered superconductivity in Th₄H₁₅ and PdHₓ respectively. Within the BCS picture, the influence of hydrogen can be understood
qualitatively as arising in coupling of optical phonons to the electron system, leading to the expectation of an isotope effect in which heavier interstitials lower $T_c$.

No isotope effect was resolved in Th$_4$H$_{15}$. The discovery shortly thereafter of a strong inverse isotope effect between PdH$_x$ and PdD$_x$ [52] generated great interest and controversy by apparently contradicting the predictions of simple BCS theory. An even larger inverse isotope effect was found for tritium in Pd [55].

More recently, experiments on hydrogenation of cuprates [56], MgB$_2$ [57], carbon-based superconductors [58, 59] and pnictides [60, 61] have been reported.

### 2.4.1 Palladium

Palladium metal is an enhanced Pauli paramagnet and becomes diamagnetic as the $d$ band is filled by absorbing H [62]. Thus it appeared that suppressing spin fluctuations by quenching the paramagnetism of Pd was the essential precondition for superconductivity in palladium [63], despite the strong reduction in the electronic density of states at the Fermi energy, $N(0)$.

#### 2.4.1.1 Critical temperature ($T_c$) dependence on H(D) concentration

*Table 2-1* summarises the reported values for $T_c$ of hydrogenated Pd. The agreement among the various reports is relatively good. Inhomogeneity of the H(D) distribution may explain the variable width of the superconducting transition across samples and techniques.
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Table 2-1: Reported values of the superconducting transition temperature at zero pressure for hydrogenated palladium.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>H(D)/Pd</th>
<th>$T_c$ (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.0</td>
<td>8.8</td>
<td>[52]</td>
</tr>
<tr>
<td>D</td>
<td>1.2</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>8.5</td>
<td>[64]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.6</td>
<td>[65]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.5</td>
<td>[66]</td>
</tr>
<tr>
<td>D</td>
<td>1.0</td>
<td>11.7</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>8.0</td>
<td>[54]</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>9.4</td>
<td>[67]</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>11.8</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>0.72</td>
<td>0.04</td>
<td>[55]</td>
</tr>
<tr>
<td>T</td>
<td>0.81</td>
<td>0.09</td>
<td></td>
</tr>
</tbody>
</table>

2.4.1.2 Pressure effect on critical temperature

Several studies have been made of the effect of hydrostatic pressure on $T_c$ of PdH$_x$ and PdD$_x$ [45, 47, 48, 66], showing that increasing hydrostatic pressure results in decreased $T_c$. Qualitatively this effect may be explained by hardening of the phonon spectrum causing a decrease in the electron–phonon coupling constant, $\lambda$ [47].

A quantitative explanation of the effect of pressure on $T_c$ has been given by Hemmes, et al. [68]. Based on band-structure calculations and new measurements of the pressure effect in PdH and PdD, they reproduced the experimental effect by including
anharmonicity and the Debye-Waller factor in the volume dependence of the electronic parts of the electron–phonon coupling constant. This model also accounts for the inverse isotope effect, in agreement with the conclusion of Ganguly [69] that anharmonicity is the root cause of the inverse isotope effect in Pd–H(D) alloys.

2.4.1.3 Critical field ($H_c$)

Critical field measurements on PdH$_x$ samples prepared by electrolysis at low temperature show that it is a type II superconductor. The upper critical field $H_{c2}(0)$ therefore depends strongly on the mean free path of electrons (limited by impurities and lattice distortions) giving a plausible explanation for the reported spread of $H_{c2}$ values. Skośkiewicz [70] reported $H_{c2}(0) = 0.18$ T, independent of the H concentration. McLachlan et al. [71, 72] reported $H_{c2}(0)$ values between 0.08 and 0.16 T, depending on the H content or the prevalence of lattice distortions.

2.4.1.4 Other properties of the Pd–H System

The lattice dynamics of a single crystal of PdD$_{0.63}$ were studied by Rowe, et al. [73]. Acoustic mode frequencies 20% lower than those of pure Pd were found. Although Rowe, et al. [73] claimed that this shift was in agreement with the observed lattice expansion, Abbenseth and Wipf [74] showed that it was about four times larger than the expected value for the expanded lattice, suggesting that hydrogen charging causes softening of the acoustic phonons. For optical modes due to D the analysis of the scattering data is not simple, as the standard lattice dynamic treatment cannot be applied to a non-stoichiometric sample [75]. Rahman, et al. [76] concluded that the Pd–H force constants are about 20% stronger than the corresponding Pd–D force constants for D/Pd = 0.63 while comparing with incoherent neutron scattering data on polycrystalline
samples with H/Pd = 0.63. This anharmonicity is the fundamental reason for the occurrence of inverse isotope effect in superconductivity in Pd–H(D) alloys [69].

The temperature-dependent resistivity of PdH$_x$ with $x = 0.995$ was measured by MacLachlan, et al. [71]. A change in the variation of the resistivity with respect to temperature at about 140 K was explained as the onset of a secondary scattering interaction of the conduction electrons with optical phonons. For temperatures less than 80 K, the experimental data were fitted to a Grüneisen function with $\theta_D = 210$ K. After desorption of hydrogen, the resistivity could be expressed in terms of a Debye spectrum with $\theta_D = 1000$ K, in the temperature range between 80 and 280 K. The latter is in near agreement with the results obtained for tunnelling experiments. MacLachlan, et al. [71] assumed that the change in resistivity with respect to temperature is proportional to the electron–phonon coupling constant ($\lambda$) and $\lambda_{\text{optical}} \approx 3\lambda_{\text{acoustic}}$ was obtained. Chiu and Devine [77] made a similar analysis of temperature-dependent resistivity for various H/Pd ratios. They concluded that $N(0)$ decreases by a factor of 6 when the H/Pd ratio is changed from 0 to 0.9.

2.4.1.5 High-temperature superconductivity in the Pd–H$_2$ system

Tripodi et al. [20, 21] claim to have repeatedly observed superconductivity in electrolytically loaded PdH$_x$ at much higher temperatures than previously reported, almost up to room temperature.

Their electrochemical system consisted of a palladium wire cathode between two plate anodes. This atypical geometry and short loading time were adopted to maximize the amount of hydrogen loaded into the palladium cathode and minimize the transport of anodically produced species to the cathode [21]. It was reported that achieving a very
high H content depended critically on controlling impurities in the electrolyte. Four-probe AC resistivity measurements (1 kHz) were made during electrolysis. The hydrogen content was stabilised with a Pd–Hg amalgam layer some hundreds of nm thick to prevent migration of H to the surface and loss by recombination. By this means, H/Pd ratios above 1 were claimed to be maintained at room temperature and room pressure [20].

The AC magnetic susceptibility measurements revealed $T_c$ values in the range 8–273 K, as illustrated in Figure 2-3. The evidence of potential superconducting phase with significant signal of imaginary component $\chi''$ at $T_c = 263.5$ K and another phase at lower temperature $T_c = 235$ K both related to PdH$_x$ zones with stoichiometry $x > 1$ [Figure 2-3 (a)]. The same sample in all measurement cycles shows a very good stability $T_c = 235$ K but compared to previous transitions the signal amplitude has decreased while the width of the superconducting transition has increased [Figure 2-3(b)]. In a test of long-term stability, the initial transition temperature of 263.5 K decreased to 261.5 K after a week of sample storage and $T_c = 160.5$ K was observed after two years of sample storage under the same conditions [78]. Evidence of flux expulsion and the Meissner effect were found for a sample with $T_c = 235$ K.
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Figure 2-3 (a, b): (a) Imaginary component of ac magnetic susceptibility of PdH$_x$ sample with stoichiometry x > 1, (b) Real and Imaginary component of ac magnetic susceptibility of PdH$_x$ at $T_c = 235$ K [20].

The electrical resistance transition curves of PdH$_x$ samples are shown in Figure 2-4 [79]. The value of $T_c = 51.6$ K is shown in plot (A) with $H_{DC} = 0$ T. The plot (B) shows a transition with $T_c$ at about 31.3 K and 18.8 K in the presence of DC magnetic field of 1.0 T. The drop in the resistance value is small suggesting that only a small portion of the sample is in superconducting state.
Figure 2-4: Superconducting resistive transition for PdH\textsubscript{x} samples. Plot (A) with $T_c = 51.6$ K with $H_{DC} = 0$ T, and plot (B) with double transition at $31.3$ K and $18.8$ K with $H_{DC} = 1$ T \cite{79}.

These results have not been reproduced by other groups and must therefore be regarded as unconfirmed. Baranowski and Debowska \cite{80} published a very negative comment on the work of Tripodi et al., which was countered by a detailed response \cite{81} listing the full bibliography of their work.

A second indication of high-$T_c$ superconductivity in PdH\textsubscript{x} comes from the work of Lipson et al. \cite{22, 23, 82}. An anomalous diamagnetic contribution to the magnetic susceptibility was interpreted as filamentary superconductivity arising in an extremely high density of hydrogen trapped in dislocation cores following transit through the two-phase region that spans the miscibility gap between the $\alpha$ and $\beta$ phases.

In searching for an explanation of this "high-$T_c$" effect in PdH\textsubscript{x} (if real), we note that gradual loss of hydrogen is imputed to be the cause of the decrease in $T_c$ during storage. This observation provides a clue as to how such high values of $T_c$ might be plausible. The Hg amalgam with which the Pd sample was coated post-hydrogenation is
presumed to prevent H from escaping the sample. Noting that the heavier isotope D is mobile at 50–75 K on a time scale of many hours [51], and at about 100 K on a timescale of many minutes [45], some hydrogen will escape during cooling from room temperature and heating from low temperatures if the surrounding hydrogen pressure is not maintained. This reality affects samples loaded electrolytically and by ion implantation. Thus, preventing hydrogen escaping by coating the Pd with a hydrogen-impermeable layer, or confinement by other means such as in dislocation cores, is conceivably a crucial factor in achieving high transition temperatures.

2.4.2 Palladium alloys

Alloying with selected elements has been used to change the electronic structure and phonon spectrum of Pd and so explore their effects on $T_c$ in particular.

2.4.2.1 Substitutional alloys

Table 2-2 summarises the reported effects on $T_c$ of alloying Pd with nearby and more distant elements. Substitution of Pd by the neighbouring elements Ni, Rh, Ag, and Pt decreases the solubility of hydrogen considerably [83]. Hydrogen implantation at low temperatures has been used to achieve non-equilibrium H concentrations and so find the concentration of an alloying element at which $T_c$ is maximum for that element $T_{c,max}$. Platinum substitution does not affect $T_{c,max}$ very much up to about 25 at.% platinum, but $T_{c,max}$ is strongly suppressed by less than 10 at.% Ni, even though metallic Ni content shares the 0.6 $d$-band hole of Pd. So, for the superconductivity of the hydrogenated material, this electronic property of the host lattice seems not to play an important role. Substituting for Pd by more than 20 at.% Ag causes the inverse isotope effect in pure PdHx to revert to normal [44].
## Table 2-2: Effect of substitutional alloying of Pd on superconducting transition temperatures.

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>Effect on $T_c$</th>
<th>Maximum $T_c$ (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Increases up to about 5 at.% Al</td>
<td>9.6</td>
<td>[44, 50, 83-86]</td>
</tr>
<tr>
<td>Ti</td>
<td>Decreases</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>Decreases &lt; 10 at.% Ni</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>Increases up to about 45 at.% Cu</td>
<td>17.0</td>
<td></td>
</tr>
<tr>
<td>Rh</td>
<td>Decreases</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>Increases up to about 30 at.% Ag</td>
<td>15.6</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>Almost constant up to about 25 at.% Pt, and then decreases</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>Increases up to about 16 at.% Au</td>
<td>13.5</td>
<td></td>
</tr>
</tbody>
</table>

When the atomic mass of the substituted noble metal was decreased, a consistent increase of $T_{c,\text{max}}$ was observed [44], suggesting that the acoustic phonon spectrum of these hydrides has a strong effect on $T_c$. When Pd$_{1-x}$Al$_x$ alloys were charged with H by implantation at low temperatures [86], a slight increase of $T_c$ was observed at low Al concentration. Implantation of H into a Pd–Ti alloys [86] revealed a decrease in $T_c$ with increasing Ti content.

### 2.4.2.2 Interstitial alloys

The strong inverse isotope effect in Pd–H(D,T) invites an inquiry as to whether $T_c$ continues to increase with increasing mass of the interstitial element. Boron, carbon and nitrogen were implanted in Pd by Stritzker and Becker [87] but reduced $T_c$, as
summarised in Table 2-3. The reason for this is evidently the differing electronic structure resulting from adding these heavier elements. H, D and T enhance the electron–phonon coupling, due to screening of the protons (deuterons, tritons) by the conduction electrons. With heavier elements, on the other hand, this coupling is reduced because the nuclei are more effectively screened by their core electrons. Thus the nuclei of B, C, and N have a relatively small pseudopotential due to their core electrons and also due to more localized valence electrons, decreasing the electron–phonon coupling. A decrease in transition temperature $T_c$ with increasing atomic number is observed experimentally. Stronger coupling can be obtained by a weakening of some palladium phonon modes as in Pd–H [73] and, possibly, in Pd–noble metal–H alloys [88], and also by increasing the pseudopotential of the rather un-screened proton interstitials.

Table 2-3: Effect of increasing interstitial mass on superconducting transition temperature of Pd–X, X = H, Pd, T, B, C, N [55, 86].

<table>
<thead>
<tr>
<th>Implanted element</th>
<th>H</th>
<th>D</th>
<th>T</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{c,\text{max}}$ [K]</td>
<td>8.8</td>
<td>10.7</td>
<td>0.09</td>
<td>3.8</td>
<td>1.3</td>
<td>&lt;0.2</td>
<td>[55, 87]</td>
</tr>
<tr>
<td>Concentration at $T_{c,\text{max}}$ (ion/Pd)</td>
<td>1</td>
<td>1</td>
<td>0.81</td>
<td>1.5</td>
<td>0.6</td>
<td>&gt;2</td>
<td></td>
</tr>
</tbody>
</table>

2.4.3 Thorium and its alloys

Pure Pd is a normal conductor, but Th itself becomes superconducting at 1.37 K. Thorium reacts readily with gaseous hydrogen at elevated temperatures, producing hydrides that are stable at room temperature. Matthias, et al. [89] and Satterth.Cb and Peterson [90] showed that the transition temperature drops below 1.1 K in the dihydride ThH$_2$. Further hydrogenation leads to a good superconductor with atomic ratio H(D)/Th $\approx$ 3.6, with crystal structure corresponding to Th$_4$H$_{15}$ and $T_c = 8.05$–$8.35$ K [2]. Dietrich, et al. [91] and Miller, et al. [92] reported $T_c$ values of 7.7–8.0 K and 8.5–9.0 K.
respectively. No isotope effect was resolved between Th$_4$H$_{15}$ and Th$_4$D$_{15}$ [2], in contrast to the prediction of simple BCS theory and contradicting the proposal that superconductivity in Th$_4$H$_{15}$ might be due metallic H(D) in the Th lattice. Metallic H should show a pronounced normal isotope, i.e., a lower $T_c$ for Th$_4$D$_{15}$. Dietrich, et al. [91] reported that $T_c$ increased sharply with increasing pressure, in contrast to PdH$_x$, and at pressures up to 28 kbar no saturation of $T_c$ occurred.

Shein, et al. [93] calculated the electronic properties of Th$_4$H$_{15}$ and compared them with those for alpha-Th and ThH$_2$. The average value of the electron–phonon coupling constant for Th$_4$H$_{15}$ was calculated to be 0.38, corresponding to a weak-coupling superconductor. No explanation was offered of the absence of an isotope effect.

Oesterreicher, et al. [94] prepared hydrides of alloys of Th with Y, Zr, La, Ce and Bi. Alloyed with La, the Th$_4$H$_{15}$ structure is stable to a composition of about Th$_{0.65}$La$_{0.35}$H$_{3.7}$. Y, Ce, Zr and Bi can substitute for Th in Th$_4$H$_{15}$ beyond Th$_{0.9}$M$_{0.1}$. Superconducting transition temperatures were found to decrease equally on substitution for Th by Y, Zr, La, Ce and Bi.

### 2.4.4 Other transition metals

Progress in high-pressure technology leading to the production of new high-pressure hydrides [95, 96] also led to the discovery of further superconducting hydrides among the transition metals.

Elemental titanium is a superconductor with $T_c$ $\sim$ 2 K and its hydride TiH$_{0.85}$ is also superconducting having a critical temperature $T_c$ $\sim$ 2.6 K [97].
Elemental molybdenum is a superconductor with $T_c = 0.92$ K. Its hydride and deuteride are also superconductors [98] and exhibit an inverse isotope effect with $T_c = 0.92$ K for MoH$_{1.27}$ and 0.94 K for MoD$_{1.26}$.

The explanation of the inverse isotope effect appears to be the same as for palladium [71], as a consequence of anharmonicity of the potential modifying the BCS electron–phonon coupling constant.

M–H systems with M = Nb and V were initially reported to be non-superconducting for temperatures above 1.2 K [79], but Antonov, *et al.* [99] established that neither Nb nor V di-hydrides showed any sign of superconductivity at $T \approx 0.35$ K.

An in-depth investigation of the Nb–H$_2$ system showed that superconductivity is suppressed below 1.3 K in the hydrogen-dissolving β-phase (mono-hydride) [100]. A comparison with Pd–H$_2$ is interesting. In both these systems H is reported to be dissolved nearly as a proton [89, 90] which acts as the strong scatterer for the screening conduction electrons. The site occupied by H interstitials differs between Nb–H (tetrahedral) and Pd–H (octahedral). As a result the energies of the H vibrational modes are much higher in Nb–H, owing to the stiffer potential of the smaller T site, and probably less favourable for superconductivity than in Pd–H. Another anomaly is that the shape of the acoustic phonon spectrum is more strongly affected by hydrogenation of Nb than Pd. Peculiarities in the acoustic spectrum of pure Nb are believed to be the reason for its high $T_c$ of 9.2 K [101-103]. The addition of hydrogen reduces these anomalies and may compensate the coupling of the optical hydrogen modes ($T_c$-enhancing mode) resulting in a suppression of $T_c$.

In Nb-based alloys containing palladium [11-13], solution of hydrogen was found to have a positive effect on $T_c$. The Nb–Pd–Mo–H$_x$ alloys shows an increase of 0.38 K
in $T_c$ by increasing $x$ to $\sim 0.2$. It is plausible that in this system the fcc host lattice having high density of octahedral vacancies due to deviation from stoichiometry, the introduction of hydrogen in these sites should lead to further enhancement of $T_c$.

An interesting effect was observed [11] in hydrogenation of Nb$_{80}$Rh$_{20}$ with hydrogen-to-metal ratio $= 0.1$, which had $T_c = 5.64$ K, compared to $T_c = 2.65$ K for the original alloy. At higher hydrogen–to–metal ratios, Nb$_{88}$Rh$_{12}$H$_{1.7-2.0}$, the observed values of $T_c$ were 0.75–0.90 K.

Antonov, et al. [99] studied the solubility of hydrogen in Nb–Rh alloys and found superconducting hydrides Nb$_{0.65}$Rh$_{0.35}$H$_{1.4}$ ($T_c = 1.8$ K) and Nb$_{0.75}$Rh$_{0.25}$H$_{1.5}$ ($T_c = 1.1$ K) that retained the crystal structures of the alloys.

### 2.4.5 Cuprates

High-temperature oxide superconductors [104, 105] display a strong dependence of $T_c$ on the crystal and defect structure. For instance, orthorhombic YB$_2$Cu$_3$O$_{7-\delta}$ ($\delta < 0.5$), with layered anisotropy is a high-temperature 92.5 K superconductor [106], whereas the tetragonal phase of YB$_2$Cu$_3$O$_{7-\delta}$ is not a superconductor above 4.2 K [107]. The main difference between these structures is unoccupied lattice sites (oxygen vacancies) and the lack of ordering of oxygen atoms along the one dimensional chains of Cu(2)–O layers [106-108].

At least one cuprate superconductor (YB$_2$Cu$_3$O$_7$) does absorb hydrogen strongly. Reilly, et al. [14] investigated the effect of hydrogen absorption by H$_x$YB$_2$Cu$_3$O$_7$ on the crystal structure, the electronic state and the superconducting properties. Hydrogen will dissolve in the oxide up to a concentration $x \sim 0.2$, resulting in a superconducting solid solution phase having $T_c \sim 94$ K slightly higher than the original oxide.
Superconducting transition temperatures for H-modified YB$_2$Cu$_3$O$_7$ are listed in Table 2-4. With increasing hydrogen content a decrease in superconducting volume fraction is observed as the solid solution is converted to a hydride phase.

Table 2-4: Superconducting transition temperature $T_c$ (K) of H$_x$YB$_2$Cu$_3$O$_7$ and the relative starting oxides.

<table>
<thead>
<tr>
<th>H$_x$YB$_2$Cu$_3$O$_7$ samples with hydrogen content ($x$)</th>
<th>$T_c$ (K)</th>
<th>Relative superconducting fraction %</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>91.0</td>
<td>100</td>
<td>Orthorhombic structure</td>
</tr>
<tr>
<td>0</td>
<td>$\alpha^*$</td>
<td>...</td>
<td>Tetragonal structure, $\alpha^*$→non-superconducting above 4.2 K</td>
</tr>
<tr>
<td>0.14</td>
<td>92.5</td>
<td>100</td>
<td>Solid solution</td>
</tr>
<tr>
<td>0.48</td>
<td>93.6</td>
<td>70</td>
<td>...</td>
</tr>
<tr>
<td>1.0</td>
<td>93.2</td>
<td>30</td>
<td>Mixed phases, <em>i.e.</em> H$_{1.0}$YB$_2$Cu$_3$O$_7$ + Hydride phases</td>
</tr>
<tr>
<td>4.0</td>
<td>$\alpha^*$</td>
<td>...</td>
<td>Amorphous hydride phase(s)</td>
</tr>
<tr>
<td>5.0</td>
<td>$\alpha^*$</td>
<td>...</td>
<td></td>
</tr>
</tbody>
</table>

The origin of the effect of dissolved H on $T_c$ can be surmised from its effect on the crystal structure. Figure 2-5 shows the lattice parameters of the expanded cell of H$_x$YB$_2$Cu$_3$O$_7$ as a function of hydrogen content $x$. The $c$ lattice parameter and, to a lesser extent $a$, increases, but $b$ remains almost unchanged with increasing hydrogen content, suggesting that hydrogen occupies sites leaving the Cu(2)–O layer chains.
unbroken along the $b$ axis which have been assumed to be important for the occurrence of superconductivity [108-110]. Hydrogen inhibits the oxygen vacancy on the $c$ or $a$ axis, or both, and is correlated particularly with Cu in the solid solution region.

![Graph showing lattice parameters of expanded cell of H$_x$YB$_2$Cu$_3$O$_7$ as a function of hydrogen content $x$.]

Figure 2-5: The lattice parameters of the expanded cell of H$_x$YB$_2$Cu$_3$O$_7$ as a function of hydrogen content $x$ [14, 103, 104].

A subsequent study [56] with infrared spectroscopy and x-ray absorption spectroscopy confirmed that H is not associated with the O atoms but is located interstitially near Cu sites and forms Cu–H bonds.

Overall, the response of this system is similar to those metals and hydrogen systems where H occupies a metal-atom coordinated, interstitial site, although no explanation of the effect of H on $T_c$ has been offered. We remark that neutron diffraction with deuterium-modified YB$_2$Cu$_3$O$_7$ would provide direct evidence of the D site and an opportunity to explore possible H isotope effects and further clues as to the mechanism by which H affects $T_c$. 
2.4.6 Magnesium diboride

Superconductivity in MgB$_2$ with $T_c \approx 39$ K was reported in 2001 [15, 16]. Following this, many known diborides were revisited and new ones prepared. In particular, Kaczorowski, et al. [111] found superconductivity in TaB$_2$ ($T_c = 9.5$ K), which was previously thought not to be a superconductor.

Bugoslavsky, et al. [17] enhanced the high-field critical current density of MgB$_2$ by implanting protons, which causes damage that increases the concentration of flux-pinning centres. There was a concomitant decrease in $T_c$ along with a broadening of the transition, the latter evidently related to inhomogeneity of the damage caused by the relatively high-energy protons. The effect of the protons on the electronic structure was not considered.

The superconducting properties of MgB$_2$ and the influence of hydrogen on these properties were studied by Zaleski, et al. [112]. Hydrogenation at 100 °C under 20 bar and 7 kbar H$_2$ pressure were reported to have essentially the same effects: uptake equivalent to MgB$_2$H$_{0.03\pm0.01}$; no resolvable change in lattice parameters and negligible change in $T_c$. Alternating susceptibility measurements on MgB$_2$ hydrogenated at 20 bar suggested that the amount of superconducting phase was much lower for the hydrogenated MgB$_2$ and the transition narrower in temperature. The hydrogen uptake was very low and independent on the pressure used and the volume of the phase with MgB$_2$-type structure remained unchanged after hydrogenation.

In contrast, Flambaum, et al. [57] succeeded in increasing $T_c$ by about 1.2 K after soaking in 10 bar hydrogen at 600 °C. The estimated uptake corresponded to MgB$_2$H$_{0.03}$. Soaking in Ar or He produced smaller increases in $T_c$. A small lattice expansion in the $c$ direction was observed. Wan, et al. [113] calculated the influence of lattice parameter on the band structure of MgB$_2$ and concluded that expansion of the
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unit cell increases $N(0)$ and thereby $T_c$. Thus the effects of He and Ar, and to some extent that of H in MgB$_2$ may be via lattice expansion.

Nakamori, et al. [114] sintered MgB$_2$ under H$_2$ and Ar at 1173 K, obtaining a small increase in unit cell volume and a 0.6 K increase in $T_c$. Li, et al. [115] hydrogenated MgB$_2$ for 2 h under 30 bar H$_2$ at 500 °C, with similar results to those of Nakamori, et al. [114]. Li, et al. [115] concluded that the increase in $T_c$ due to H absorption was caused by (i) interstitial H atoms having no effect on the shape of the Fermi surface and $N(0)$ and (ii) enhanced $E_{2g}$ vibration and intraplane B interaction. We remark that this explanation is at odds with the profound effect that uptake of interstitial H has on the band structures of other metals.

Sandu, et al. [116] loaded tritium into MgB$_2$ at room temperature from an atmosphere of T + N$_2$. A small but significant increase in the c lattice parameter and a decrease in a were observed, along with an initial small increase in $T_c$ (by about 0.3 K) that slowly disappeared as the T decayed to He.

The effect of hydrogen on MgB$_2$ is evidently real, and positive in that $T_c$ is enhanced, albeit a small one.

2.4.7 Carbon-based superconductors

Carbon in its various pure forms has not been found to super-conduct, except for carbon nanotubes, although numerous carbon-based or carbon-containing materials have shown superconductivity. The earliest carbon-based superconductors to have been discovered were binary transition metal carbides with transition temperatures up to 11.1 K [117], among the highest achieved before the discovery of high-$T_c$ oxydcuprates and fullerenes [118]. Superconductivity has been observed in fullerenes, polycrystalline C$_{60}$
and C_{60} films doped with alkali metals. Potassium-doped C_{60} exhibited a transition temperature of 18 K [125]. Transition temperatures up to ~ 33 K were observed [119] by adjusting the separation of the C_{60} molecules using intercalated alkali metals. Interest has also developed in the boro-carbides REM_{2}B_{2}C, RE=Y or Lu and M= Ni or Pd, having transition temperatures up to ~ 22 K [120-122].

Superconductivity has been found in graphite intercalation compounds (GICs), but with transition temperatures well below 1 K [88, 123]. Later, it was found that the transition temperatures of Li- and Na-intercalated GICs could be increased by intercalation under pressure, but \( T_c \) did not exceed 4 K [124, 125]. Intercalating divalent alkaline earth metals like Ca and Yb produced transition temperatures of the GICs that were significantly enhanced [126]. The substitution of about 3% B into C sites in diamond results in a Type II superconductor with transition temperature below 4 K [127]. Further work on diamond films suggests that the transition temperature could be varied from ~ 1 to 10 K depending on the range of boron doping [128]. It has been predicted on the basis of electron–phonon pairing that the transition temperature could rise to 55 K with heavy boron doping of 20–30\% and for that reason super-hard diamond-like BC_{5} has been synthesized [129] with a boron content of 16.7\%. This has been predicted to have a transition temperature of about 45 K [130], but, it remains to be seen if these high transition values will be achieved.

Carbon nanotubes exhibit superconductivity at 15 K [131] and at the same time, a report of \( T_c \sim 0.55 \) K was made for single-walled carbon nanotube ropes [132]. The discrepancy between the \( T_c \) values is attributed to the former being zigzag tubes and the latter being armchair tubes, a reference to how the tubes are rolled [133-135]. A carbon nanotube connecting two superconductors explains the bound electron–hole states that carry a super current which was analysed from the tunnelling spectra [136]. Tang, et al.
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[135] observed superconductivity in 4 Å single-walled carbon nanotubes (SWCNT) with a critical temperature of 15 K. They also observed that the smaller the diameter of the carbon nanotube, the higher the superconducting temperature. The possible explanation for this enhancement is the greater curvature of the tube increases the interaction between the electron and the lattice vibrations (phonons) which is the essential property for superconductivity. The hydrogenation of single-walled nanotubes (SWNT) as a function of hydrogen concentration has been investigated with extensive first principles calculations [58]. Addition of hydrogen on nanotubes gives rise to many properties which can mediate important applications in molecular electronics. One of the important effects of hydrogenation on SWNTs is the formation of metallic square or rectangular cross-section nanotubes with a high density of states at the Fermi level from the zigzag nanotubes [137].

2.4.8 Iron-based superconductors

The discovery of a new class of superconductors by Japanese researchers led by Hideo Hosono in 2008 reignited research in superconducting materials. Iron-based superconducting materials have a relatively higher critical temperature than the conventional low temperature superconductors [138]. Along with many similarities to the high-$T_c$ cuprates, the proximity of antiferromagnetism to superconductivity in these semi-metallic materials has attracted much attention. Many chemical substitutions are possible in these ternary or quaternary compounds. This feature enables the superconducting properties to be moulded for commercial technologies and also opens a new pathway to understanding the origin of the superconductivity phenomenon.

These superconductors can be classified into four major types according to their base stoichiometries and crystal structures. The first type is "1111", exemplar LnFeAsO,
where Ln represents lanthanides and oxygen is partly substituted by fluorine, with ZrCuSiAs-type tetragonal crystal structure (P4/mmm space group). This consists of alternating positively and negatively charged Ln–O, and Fe–As layers along the c axis. The Ln$_2$O$_2$ layer represents an insulating charge reservoir layer, while the Fe$_2$As$_2$ layer acts as the active block of conducting layer. The sheet of Fe$^{+2}$ ions lies in between LnOAs$^{-2}$ ionic blocks of the LnFeAsO structure. The highest superconducting transition temperature $T_c$ obtained in 1111-type is ~ 57 K. The second "122" type has exemplar AFe$_2$As$_2$, in which A corresponds to a divalent alkali-earth ion viz. Ba, Sr, Ca. This structure shows antiferromagnetic ordering similar to the 1111 type [139] as first reported in BaFe$_2$As$_2$. The highest superconducting transition temperature of the material itself or the highest $T_c$ obtained by doping or substitution in a material of that type is ~ 38 K. The third "111" type, exemplar LiFeAs, has the Cu$_2$Sb-type structure. This type is extremely sensitive to sample preparation and the maximum $T_c$ achieved in this particular type is ~ 18 K [140-142]. The last "11" type, exemplar α-FeSe [143], is structurally one of the simplest, having a α-PbO type structure and the highest superconducting critical temperature observed in this type is ~ 14 K.

Doping at different sites in all four types of iron based superconductors is listed in Table 2-5. Dopants such as Rh, Ir, Pd, and Ru have been substituted at iron sites but most led to insensitive suppression of transition temperature that countered the proposed s-wave pairing symmetry [144-147]. The creation of As vacancies as well as the addition of dopants at iron sites demonstrated that these superconductors can tolerate some extent of in-plane disorder in the FeAs conducting layer.
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Table 2-5: List of iron pnictides belonging to four different types and maximum critical temperature achieved.

<table>
<thead>
<tr>
<th>Type of superconductor</th>
<th>Example</th>
<th>(x) value</th>
<th>Preparation method</th>
<th>$T_c$ (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘1111’-LnFeAs(O$_{1-x}$F$_x$)</td>
<td>Ln=La, Ca, Nd, Sm, Gd</td>
<td>0.11, 0.16, 0.12, 0.2, 0.17</td>
<td>Solid State</td>
<td>26, 41, 52, 55, 36</td>
<td>[138, 148-152]</td>
</tr>
<tr>
<td></td>
<td>Ln=Pr, Tb, Dy</td>
<td>0.11, 0.1, 0.1</td>
<td>High Pressure</td>
<td>52, 46, 45</td>
<td>[138, 148, 153, 154]</td>
</tr>
<tr>
<td>‘122’-(A$_{1-x}$B$_x$)$_2$Fe$_2$As$_2$</td>
<td>A=Ba; B=K</td>
<td>0.4</td>
<td>Solid State</td>
<td>38</td>
<td>[139]</td>
</tr>
<tr>
<td>‘122’-A(Fe$_{1-x}$B$_x$)$_2$As$_2$</td>
<td>A=Ba; B=Ni, Rh, Pd</td>
<td>0.096, 0.057, 0.053</td>
<td>Flux</td>
<td>20.5, 24, 19</td>
<td>[144-147, 155]</td>
</tr>
<tr>
<td></td>
<td>A=Sr; B=Rh, Ir, Pd, Ru</td>
<td>0.25, 0.43, 0.15, 0.4</td>
<td>Solid State</td>
<td>21.9, 24.2, 8.7, 11.8</td>
<td></td>
</tr>
<tr>
<td>‘111’-AFeAs</td>
<td>A=Li$_{1-x}$</td>
<td>0.2, 0.4</td>
<td>High Pressure</td>
<td>16, 18</td>
<td>[140-142]</td>
</tr>
<tr>
<td>‘11’-αFeSe</td>
<td>…</td>
<td></td>
<td>Solid state</td>
<td>8</td>
<td>[143]</td>
</tr>
</tbody>
</table>

Hydrogen has played a role from the start of this exciting new field, both in the synthesis process and the final material. Hanna, et al. [60] proposed a high-pressure synthesis method to induce superconductivity in 1111-type iron arsenides. Compounds such as CaFeAsF$_{1-x}$H$_x$ ($x=0-1.0$) and SmFeAsO$_{1-x}$H$_x$ ($x=0-0.47$) were synthesized using high pressure to form hydrogen-substituted 1111-type iron-arsenide superconductors. CaFeAsF$_{1-x}$H$_x$ was found to be non-superconducting, but a maximum...
critical temperature $T_c = 55$ K was observed for SmFeAsO$_{0.8}$H$_{0.2}$ suggesting that the hydrogen ($H^{\text{\textsuperscript{\downarrow}}}^{-}$) substitution to anion ($O^{\text{\textsuperscript{\downarrow}}}^{-}$) site supplies electrons to FeAs layer, giving rise to superconductivity. Hanna et al. [156] used the method of thermal annealing to eliminate incorporated hydrogen from non-superconducting CaFeAsO$_{0.8}$H$_{0.2}$ at 553 K for 72 h under a helium gas flow resulting in bulk superconductivity with $T_c = 29$ K which is higher than the reported $T_c = 25$ K for AFeAsF (A = alkali-earth) synthesized using direct doping techniques [157-159]. Parasharam, et al. [160] synthesized the heavy lanthanide 1111-type ErFeAsO$_{1-x}$H$_x$ superconductor by the hydrogen doping method and observed $T_c = 44.5$ K. Muraba et al. [161] reported an enhancement of the three-dimensional electronic structure in 1111-type CaFeAsH, which is induced by Co substitution at the Fe site. A maximum $T_c = 23$ K was observed in CaFe$_{0.91}$Co$_{0.09}$AsH, which was fabricated using a high-pressure solid-state reaction method.

Nakamura and Machida [162] have tried to explain the origin of $T_c$ enhancement due to hydrogen doping. They concluded that in 1111-type LaFeAsOH$_x$ superconductors the most stable location of hydrogen atoms is near Fe sites and that makes the crystal structure more suitable for superconductivity. Electron doping due to hydrogen may be also related to the enhancement and to clarify the origin of $T_c$ enhancement due to hydrogen doping, it is important to investigate the position of hydrogen atom inside the crystal.
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[146] X.Z. Fei Han, Peng Cheng, Gang Mu, Ying Jia, Lei Fang, Yonglei Wang, Huiqian Luo, Bin Zeng, Bing Shen, Lei Shan, Cong Ren, and Hai-Hu Wen, Superconductivity and phase diagrams of the 4d- and 5d-metal-doped iron arsenides SrFe$_{2-x}$M$_x$As$_2$ (M=Rh,Ir,Pd) Phys. Rev. B, 80 (2009) 024506.


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Materials and Methods

3.1 Materials

3.1.1 Palladium

Palladium is a rare and lustrous silvery-white metal discovered by William Hyde Wollaston in 1803. It has atomic number 46 (Group 10) and atomic mass 106.42(1) u. The electronic configuration of Pd is [Kr] 4d\(^{10}\). It has a face-centered-cubic (FCC) crystal structure with space group Fm\(_{3}\)m, and a lattice parameter of 3.8907 Å at 25 °C. At 25 °C it has a coefficient of linear thermal expansion of 11.8 μm/(m.K). The resistivity of highly pure Pd at room temperature is 105 nΩ.m.

For this project Pd metal wire (0.5 mm diameter, 99.95%) was purchased from Goodfellow Metals Limited (UK).

3.1.2 Hydrogen

Hydrogen has atomic number 1 and atomic mass 1.00794 u. There are three isotopes of hydrogen: protium, \(^1\text{H}\), deuterium (D), \(^2\text{H}\), and tritium (T), \(^3\text{H}\). The natural abundances of protium and deuterium are 99.98% and 0.015% respectively. Tritium is radioactive with a half-life of about 12.5 years.
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For this project protium with purity 99.99% was purchased and stored as metal-hydride in LaNi$_5$. The desorbed gas was considerably purer owing to gettering of water and oxygen by the highly reactive powdered LaNi$_5$. Deuterium with purity 99.99% was purchased, stored and supplied in the same way.

3.2  **Experimental apparatus and methods**

Although both manometric and gravimetric instruments were available for this project, a manometric Sieverts apparatus (§2.3) was used to load the samples so that measurements of resistance could be made under hydrogen pressure. The Sieverts apparatus is shown schematically in **Figure 3-1**.

![Figure 3-1: A simple generalized Sieverts hydrogenator [1, 2]. To measure an absorption isotherm, hydrogen gas is in $V_{ref}$ at measured temperature and pressure is allowed to the sample cell via valve S. The amount of absorbed hydrogen is then calculated from the final pressure in the system and the temperatures of hydrogen gas in both volumes using Eqn (2.1).](image-url)
A special sample cell with electrical feedthroughs was constructed, as shown in Figure 3-2. Originally this consisted of a 316 stainless-steel tube 10.3 mm ID × 12.7 mm OD welded to a Swagelok VCR fitting at the top and welded shut at the bottom. The pressure rating of the cell was 100 bar at 300 °C, or better. The cell was able to be heated in a furnace and transferred to a helium cryostat for measurements at cryogenic temperatures while keeping the connection to the gas manifold and therefore maintaining and continuously monitoring the hydrogen pressure. To minimize the time required to cool the sample in the cryostat, a later version had a 660 stainless steel (high-strength alloy) lower section with 0.5 mm wall thickness.

Figure 3-2: Palladium sample sitting inside the sample holder.

The cryostat used was a Cryogenics Limited Cryofree closed-cycle refrigerator with a base temperature of 4 K. The cryostat has a superconducting solenoid with a maximum magnetic field of 85 kOe (8.5 T).
Figure 3-3: Shows the entire system.

The samples consisted of approximately 80 mm lengths of 0.5 mm Pd wire wound onto an alumina former. Copper wires were spot-welded to the sample and its resistance was measured by a four-probe method to minimize systematic errors from lead resistance. A platinum thermometer was mounted in close proximity to the sample. The thermometer temperature value was obtained by measuring its resistance and subsequently its correspondent temperature value was calculated by using the standard DIN IEC 751 Temperature/Resistance table for platinum sensor.

Direct-current resistance measurements were made using an Agilent 34970A multimeter. The resistivity $\rho$ of the sample was then obtained from the resistance $R$ using

$$R = \rho \frac{L}{A}$$

(3.1)
where $L$ and $A$ are the length and cross-sectional area respectively of the wire. All measurements were made using LabVIEW 8.2 software to control the multimeter.

After connecting the electrical leads, the sample was loaded into the sample cell and sealed. The sample was heated by placing the lower end of the cell in a tube furnace. Before the initial use and between experiments, each sample was heated at 500 °C for 8 hours to relieve stresses. These were expected to be minimal because the sample did not enter the (incoherent) two-phase region during hydrogenation at 300 °C, thus avoiding dislocation generation.

Loading with hydrogen took place at approximately 300 °C, up to a pressure of approximately 100 bar. The sample was allowed to equilibrate at 300 °C for at least 2 hours, then cooled. Under isochor conditions, at room temperature the pressure dropped to approximately 80 bar and at the lowest temperature achieved (approximately 40 K), 25 bar. For later measurements the pressure was maintained as close to 100 bar as could reasonably be achieved by leaving the sample open to the pre-heated metal-hydride H or D source. Figure 3-4 shows pressure versus composition isotherms for Pd-H(D) system at different temperatures including the critical region [3-5]. A 40-K isotherm has been extrapolated using the fact that all isotherms shown converge quite closely on a single point at H/Pd = 1. At 300 °C and about 100 bar of gas pressure, the system is in the pure beta-phase region. Even when cooled under isochor conditions, the locus of the system remains in the beta-phase region. In other words, hydrogen can only be gained, not lost, during cooling. At 100 bar and 40 K, the hydrogen-to-metal ratio is very close to 1. It should be noted, however, that these are equilibrium isotherms, whereas the measurements to be reported in Chapter 4 are dynamic.
Figure 3-4: Pressure composition isotherms of Pd-H and Pd-D system at different temperatures [3-5] plus predicted 40-K isotherm.

A very recent model [6] of hydrogen absorption by Pd suggests that the hydrogen-to-metal ratio at 100 bar and 40 K is 0.95, rather close to the rough estimate based on Figure 3-4: Pressure composition isotherms of Pd-H and Pd-D system at different temperatures [3-5] plus predicted 40-K isotherm. Rapid cooling of the sample turned out to be essential for observing the superconducting transition. The cooling rate was limited by the cooling power of the cryostat. A helium-bath cryostat with higher cooling power was not available because there is no local liquid helium supply. The sample was therefore pre-cooled by immersion of the lower part of the cell in liquid nitrogen immediately after extraction from the furnace.

3.3 Sample characterisation
At 300 °C and 100 bar the sample is pure β phase. As the temperature falls the two-phase region is avoided and the sample arrives at room temperature having absorbed more hydrogen and still in pure β phase. To desorb, therefore, the two-phase region must be traversed, involving formation of the α phase and creation of misfit dislocations. This "reverse activation" process is slow. The amount of hydrogen in the sample is hard to measure by the Sieverts technique when the sample cell incorporates a temperature gradient and therefore a density gradient, but can be fairly well estimated from x-ray diffraction. In this case the sample was sufficiently stable to be x-rayed. **Figure 3-5** shows the results, obtained on a Panalytical Empyrean diffractometer in transmission mode. The initial lattice parameter of 4.05 Å corresponds to H/M = 0.7. The slow passage through the two-phase region to pure α phase and Pd over 6 hours is apparent.
Figure 3-5: Lattice parameters with respect to time after forming palladium hydride. Sample prepared above the thermodynamic critical point and the x-ray diffraction measurements taken at room temperature and pressure.

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Discovery of High-Temperature Superconductivity in the Palladium-Hydrogen (Deuterium) System

4.1 Introduction

Early in the project, measurements of the resistivity of a sample hydrogenated with protium at 300 °C and cooled to low temperature showed no indication of superconductivity. It was then found that rapid cooling followed by rapid heating sometimes induced a transition, indicated by the resistance of the sample being zero at the lowest temperature within the capability of measurement. Subject to demonstrating that this was not an artefact of the instrumentation or methodology, zero resistance indicates superconductivity through the entire sample, in contrast to previous reports of partial high-temperature superconductivity in PdHₓ [1-4]. The goals of the experimental work since those earliest hints of success have been to (i) make the measurements more repeatable, (ii) repeat the measurements with deuterium to observe any isotope effect and (iii) repeat the measurements in a magnetic field to switch off the superconductivity. Positive outcomes for the second and third goals would be strong confirmation that the phenomenon observed is superconductivity through the entire sample.
4.2 Results

4.2.1 Electrical resistivity measurements

4.2.1.1 Pure Pd

Figure 4-1 shows the resistivity as a function of temperature for pure Pd measured during slow cooling then during rapid heating. This measurement is important for two reasons. First, it shows no sign of any temperature range in which the apparent resistance of the sample is zero. The results reported in the succeeding sections which exhibit a zero-resistance range at the lowest temperatures are therefore unlikely to be artefacts of the measurement. Second, the difference between the two measurements shows that there is a lag in the temperature indicated by the thermometer adjacent to the sample relative to the sample itself, because the resistance is higher than it should be at a given temperature when heated rapidly.
4.2.1.2 Slow-cooled and slow-heated PdH/D$_x$

Palladium wire samples were loaded with hydrogen and deuterium gas at approximately 300 °C up to a pressure of approximately 100 bar for two hours. After cooling slowly (ramp rate 1 °C/s) to approximately 30 K, each sample was heated slowly (ramp rate 1 °C/s) while its resistance was measured. Figure 4-2 shows the plotted data for palladium hydride and deuteride samples. Compared to pure Pd the normal state resistance in the hydride samples is high and there is no suggestion of a zero-resistance state.
4.2.1.3 Calibration of dynamic temperature

The temperature of the sample during fast heating was calibrated by measuring a piece of Cu wire with the same dimensions as the Pd samples during slow cooling and heating and during fast heating, both under the same conditions of hydrogen pressure used for PdH$_x$. Figure 4-3 shows the fitted resistance values of the pure copper wire with respect to temperature. Under the given conditions of the Pt-100 sensor installed next to the copper wire has shown quite reasonable results. The sensor is actually keeping up with the change in temperature as expected, to within several kelvin.
Figure 4-3: Resistivity of pure copper wire measured during slow cooling (green curve) and heating (red curve) and during fast heating (black curve) under the same conditions of temperature and pressure as the palladium sample.

4.2.1.4 Observation of high-temperature superconductivity in PdH/Dx

After early trials (summarised in Chapter 5), a measurement routine was adopted that gave a reasonable success rate in observing the superconducting transition, although the results both for the transition temperature and the behaviour of the resistivity in the normal state initially varied considerably. The sample was heated to approximately 300 °C and then the hydrogen pressure was increased to approximately 100 bar to hydrogenate it. After 2 hours the sample cell was removed from the furnace and quenched in a small dewar of liquid nitrogen temperature. After about 1.5 minute the cell was transferred to the helium cryostat, where it was cooled to a temperature of about 50 K in about 1 minute with the original cell or to about 40 K in about 40 seconds.
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with the later version that had lower thermal mass. Resistance measurements were made while the sample was heated quickly to room temperature, taking about 45 minutes in the old cell and 30 minutes in the later version. The time line of the experimental procedure can be seen in Figure 4-4.

Figure 4-4: Timeline of the experimental procedure.

The results of several successful trials with the original cell and protium are shown in Figure 4-5. A very sharp increase of the resistivity from zero was observed between 50 and 60 K. About 6 out of 10 attempts exhibited the transition. The superconducting critical temperatures, measured by where the resistivity becomes zero, were 53.3 K, 54.2 K, 56.2 K and 58.0 K respectively.
Figure 4-5: Electrical resistivity versus temperature measurement of palladium hydride samples. The data were recorded during fast heating of the samples up to room temperature.

Resistivity measurements with the original cell and deuterium are shown in Figure 4-6. The samples were loaded following the same procedure as for protium. Values of the transition temperature were higher than with protium: 57.6 K, 58.1 K, 60.1 K and 61.4 K. About 7 out of 10 attempts exhibited the transition. Interestingly, there was much less variation in both the transition temperature and the temperature variation of the resistivity in the normal state compared to protium.
Figure 4-6: Electrical resistivity versus temperature measurement of palladium hydride samples. The data were recorded during fast heating of the samples up to room temperature.

In order to observe the superconducting transition it was necessary to compromise between the speed with which the quench and measurements were made and the lowest temperature reached. With the original cell a minimum temperature of about 50 K gave a reasonable chance of seeing the superconducting transition. With the later version having a lower thermal mass, the minimum practical temperature was about 40 K. The procedures for loading the sample with protium/deuterium, quenching and measuring its resistance remained the same.

Figure 4-7 shows the resistivity measurements made with protium in the modified sample cell. About 8 out of 10 attempts exhibited the transition. The observed transition temperatures were much the same, but the range in which the sample had zero resistance extended to lower temperatures. The transition temperatures and the
temperature dependence of the normal-state resistance were both less variable than with the original cell, apparently because of faster cooling.

Figure 4-7: Electrical resistivity versus temperature measurement of palladium hydride samples. The data were recorded during fast heating of the samples up to room temperature (new cell).

Resistivity measurements with the modified cell and deuterium are shown in Figure 4-8. About 9 out of 10 attempts exhibited the transition. The reason for the wider variation in normal-state resistance is unknown and may reflect variations in the cooling or heating rate. It is apparent that the samples with comparatively low transition temperature seem to have higher normal state resistivity just above the transition, suggesting stronger electron–phonon coupling, although it could also reflect the high concentration dependence of the residual resistivity [5, 6].
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Figure 4-8: Electrical resistivity versus temperature measurement of palladium deuteride samples. The data were recorded during fast heating of the samples up to room temperature (new cell).

4.2.1.5 Inverse isotope effect

The superconducting transition temperatures achieved during my experiments are listed in Table 4-1 and graphed in Figure 4-9. The number of experiments has been done and the procedure has been made in order to observe superconducting transition in Palladium hydrogen (deuterium) system. The highest achieved superconducting transition temperature $T_c$ in PdH$_x$ was $58.0$ K while in PdD$_x$ it was $61.4$ K.

Table 4-1: List of transition temperatures observed for palladium-hydrogen-deuterium system using old and new sample cell.

<table>
<thead>
<tr>
<th>Number of Experiments</th>
<th>Hydrogen</th>
<th>Deuterium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Old sample cell</td>
<td>New sample cell</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
An inverse isotope effect is observed: the average $T_c$ for PdH, is approximately 55 K while for the heavier isotope, PdD, the average $T_c$ is approximately 60 K. This is the opposite of the prediction of classic BCS theory, but in line with the experimental finding of an inverse isotope effect for low-temperature superconductivity in this system, as described in Chapter 2.

Figure 4-9: Inverse isotope effect in palladium-hydrogen-deuterium system.
4.2.1.6 Effect of magnetic field on $T_c$

Figure 4-10 shows a representative set of data for PdD$_x$ samples under high hydrogen pressure in a uniform applied magnetic field of strength up to 4 Tesla. The samples were prepared by following the usual procedure (§2.3) and the resistivity data were recorded while heating to room temperature as usual, the only difference being the presence the magnetic field. There was no evidence of the transition to zero resistance in any of the fields applied, indicating that the superconducting transition was suppressed in the temperature range of the experiments. This result strongly supports the conclusion that the transition in the resistivity is in fact a superconducting transition.

Figure 4-10: Magnetic field effects on the transition temperature in palladium deuteride samples cooled and heated rapidly.
As the sequence beginning with Figure 4-5 shows, the resistivity at temperatures approaching room temperature varies considerably, while it is better behaved below about 100 K. As a first step to uncovering any systematic trend, a series of experiments was carried out to test the influence of the initial conditions. Figure 4-11 suggests that there is a correlation between the initial pressure and the resistivity just above $T_c$, which is reasonable since higher pressure introduces more H(D) into the lattice, causing more electron scattering.

![Graph: Starting pressure versus transition temperature versus electrical resistivity at higher temperature.](image)

**Figure 4-11:** Starting pressure versus transition temperature versus electrical resistivity at higher temperature.
Chapter 4. Discovery of High-Temperature Superconductivity in the Palladium-Hydrogen (Deuterium) System

The more interesting result from Figure 4-11 is that a lower resistivity just above $T_c$ is correlated with a higher value of $T_c$.

4.3 Summary

When hydrogenated at about 300 °C and 100 bar hydrogen (deuterium), cooled rapidly to about 40 K and heated rapidly to room temperature, PdH(D)$_x$ sometimes exhibited a sudden transition from zero resistivity to roughly the normal-state value in the range 55–60 K. The transition was never observed during slow heating and a measurement made with copper wire that was treated in exactly the same way as the Pd wire showed no unusual features. Faster cooling and heating, made possible by a redesigned tail with lower thermal mass on the sample cell, increased the frequency with which the transition was observed. Nearly 100% of trials with deuterium loading in the modified sample cell produced the transition. In the next chapter, these experimental results will be discussed and interpreted.
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Chapter 5. Discussion and Interpretation of Experimental Results

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Discussion and Interpretation of Experimental Results

The most important point to discuss is whether the observed superconducting transition is real. The next point is then why the transition is observed only under dynamic conditions. Finally, an explanation of the superconductivity at such high temperatures (55–60 K) is needed.

5.1 Are the results real?

Four pieces of evidence point convincingly to the observed transition being real and not an artefact of the experimental apparatus or methodology:

1. Measurements on copper wire treated exactly the same as the Pd wire (Figure 4-3) showed a very smooth variation with temperature and no anomaly. The resistivity measured during fast heating differed from that measured during slow heating minimally, indicating a small temperature difference between the sample and the thermometer under dynamic conditions. This measurement proved that the apparatus worked very well.

2. Whenever the transition was observed, the resistance was zero within resolution at temperatures below 55–60 K. This could only be because either
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(i) a sufficient volume fraction of the sample was superconducting to give overall zero resistance, or (ii) a short-circuit sometimes occurred between the voltage-sensing wires somewhere, always in the same temperature range.

3. Repeating the experiments with deuterium instead of hydrogen led to the same transition being observed, but always at a higher temperature (Figure 4-9). It is unreasonable that this isotope effect could be an artefact of the experiment. Therefore possibility (ii) above should be discarded.

4. The transition to zero resistance was never observed when the experiments were repeated with a magnetic field above 1 kOe applied to the sample (Figure 4-10). It is unreasonable that this effect could be an artefact of the experiment owing to possibility (ii) above.

Once we accept that superconductivity really has been observed at 55–60 K, major questions are (i) why it was never observed when the sample was cooled and heated slowly and (ii) why was it not always observed when the sample was cooled and heated quickly.

5.2 Why are rapid cooling and heating necessary?

Loss of hydrogen from the sample has been given as a reason for variable $T_c$ observed reported for PdH(D), in the literature, but in the experiments reported in Chapter 4 the hydrogen (deuterium) pressure was always maintained high enough during cooling for the sample to remain in the pure $\beta$ phase, and in fact to gain hydrogen as it cooled (Figure 3-4). Less hydrogen would diffuse out of the sample during rapid heating compared to slow heating, but less hydrogen would have diffused into the sample anyway during rapid cooling compared to slow cooling. While the
transition to low-temperature superconductivity at about 10 K is very sensitive to the actual H(D) concentration in the sample (Table 2-1: Reported values of the superconducting transition temperature at zero pressure for hydrogenated palladium.), the transition to high-temperature superconductivity seems to be either observed or not observed, with a quite small relative variation in the value of $T_c$. Variable H(D) concentration probably accounts for the variation in the measured $T_c$ (several K in 50-odd K over many trials), but prevention of hydrogen loss from the sample is not the mechanism by which rapid cooling followed by rapid heating causes (or allows) the transition to appear.

5.3 **Why is quenching from high temperature necessary?**

The most logical scenario consistent with the facts is that rapid cooling quenches-in a high-temperature hydrogen configuration that is conducive to high-temperature superconductivity, and rapid heating preserves this state while the measurement takes place.

5.4 **Why is the resistivity so variable?**

Another aspect of the experimental results that needs explanation is the wild variation of the resistivity at high temperatures. The measurements on Cu wire show that this variability is real and not an artefact of the measurements. The extra electron scattering caused by interstitial H(D) has a very big effect on the resistivity (Figure 4-2), so this observation perhaps indicates an inhomogeneous state in which the local hydrogen configuration fluctuates.

*Figure 5-1* illustrates some unsuccessful trials, *i.e.* those in which the superconducting transition was not observed. Once again, the resistivity varies wildly
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with temperature, and between trials. Once again, this could indicate an inhomogeneous state, but one in which the sample as a whole does not reach a state of zero resistance.

Figure 5-1: Electrical resistivity measurement of palladium hydride and palladium deuteride samples – unsuccessful trials. The data were recorded during fast heating.

It is worth remembering that the resistance of a macroscopic sample will be zero if there is a continuous network of superconducting material between the two ends, even if the majority of the sample remains normal. The somewhat random occurrence or non-occurrence of a transition to zero resistivity could indicate that the superconducting network is continuous or broken, like the percolation phenomenon \[1\] in which the gross conductivity of a three-dimensional network of conducting elements is suddenly lost at a critical fraction of broken connections.

A further point is that in all cases where the sample was cooled and heated quickly (Figure 4-5 – Figure 4-8, Figure 5-1), the resistivity at room temperature was
no more than about half its equilibrium value (Figure 4-2), whether or not the superconducting transition was observed. This shows that the sample was always very far from equilibrium, even at room temperature, after rapid cooling and heating. It would be interesting to measure the dynamic resistivity to higher temperatures to find where it approaches the equilibrium value as diffusion speeds up.

5.5 **Qualitative interpretation of the experiments**

Cooling and heating slowly produces the well-known low-temperature superconducting state at around 10 K for a hydrogen-to-metal ratio of 1, surveyed in detail in Chapter 2. Low-temperature superconductivity in this system is associated with occupancy of octahedral interstitial sites. This is known from neutron diffraction measurements with the deuteride [2], which show convincingly that D (and presumably H) occupy octahedral interstices in the Pd lattice at and below room temperature. In fact ordering of the octahedral D occurs at temperatures below about 100 K [2], down to about 50 K, although on time scales much longer than that of the present experiments. The influence of D ordering – or its absence – on the low-temperature superconductivity is not known. We can conclude that the high-temperature hydrogen configuration that is frozen-in by cooling must differ somehow or be prevented from transforming to the low-temperature state.

The variability in the transition temperature and resistivity above $T_c$ when the sample was cooled and heated quickly suggests that the configuration of hydrogen at about 40 K (the approximate base temperature of the dynamic measurements) is very sensitive to the actual conditions and cooling rate. From neutron diffraction it is known that quenching the sample prevents D ordering, and so the possibility that the higher value of $T_c$ comes about because of the absence of D ordering needs to be considered.
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Rapid heating would avoid ordering while the sample remained below 100 K. It would be surprising, however, if higher values of $T_c$ were not observed in previous work, since cooling times from room temperature to 40 K and below comparable to, even faster than the cooling time in the present experiments would have been reasonable. In this regard it should be noted that the cooling power of the closed-cycle refrigerator used for this work is much lower than the cooling power of a conventional liquid-He cryostat.

The other possibility is that the high-temperature hydrogen configuration is not octahedral, and indeed it has been proposed [3] that significant tetrahedral D occupancy occurs at 300 °C. In this case it is feasible that some tetrahedral H(D) is preserved at 40 K by rapid cooling. The need for rapid heating to observe the superconducting transition is then easy to understand: the relatively high mobility of D would drive the system towards the equilibrium configuration, which is (ordered) octahedral occupancy.

The variability of the resistivity between trials makes it impossible to carry out a quantitative analysis of the experimental data based on the theory summarised in Chapter 1. Recalling Eqn (1.26),

$$\lambda = \frac{N(0)\langle I^2 \rangle}{M \langle \omega^2 \rangle} = \frac{\eta}{M \langle \omega^2 \rangle}$$

the electron–phonon scattering matrix element $\langle I^2 \rangle$ must vary wildly if the resistivity does. Therefore it is not possible to estimate $\lambda$ from the experimental data.

It is possible to consider if tetrahedral interstitial occupancy could lead to enhanced superconductivity, by comparing the relevant properties calculated for stoichiometric PdH$_{oct}$ and PdH$_{tet}$. Figure 5-2 shows the dependence of the electronic energies of these two systems at zero temperature on the lattice parameter, excluding the
zero-point energy. These unpublished calculations were performed by Dr Timothy Gould using VASP [4-7]. The important conclusion from these calculations is that if the lattice can be expanded sufficiently, then the tetrahedral hydride $\text{PdH}^{\text{tet}}$ is more stable than the octahedral hydride. Adding the zero-point energy reverses the order of stability, so that the octahedral hydride becomes more stable. This is because the potential of the smaller $t$ site is stiffer. The energy differences are small enough that some $t$ occupancy is likely at high temperatures owing to thermal expansion of the lattice.

![Graph](image)

Figure 5-2: Electronic energies of $\text{PdH}^{\text{tet}}$ (red curve) and $\text{PdH}^{\text{oct}}$ (green curve) at 0 K versus lattice parameter. The $M$ index refers to the saddle point on the cube diagonal (blue curve). Unpublished calculations by Dr. Timothy Gould.

Allen and Dynes [8] conclude that to increase $\lambda$ it is more important to increase $\eta$ than to decrease $\langle \omega^2 \rangle$. Lowering $\langle \omega^2 \rangle$ owing to soft phonon modes, say, does increase $\lambda$, but it also decreases $\omega_{\text{log}}$ in Eqn (1.28). Stated in another way, the
dependence of $\lambda$ on the average phonon frequency is complicated, and increasing $\langle \omega \rangle$ would not necessarily decrease $T_c$.

If tetrahedral occupancy is responsible for the high-temperature superconductivity, the phonon spectrum for the superconducting regions would be quite different from that in regions of only octahedral occupancy, because of the much stiffer H potential in the smaller $t$ sites. Figure 5-3 and Figure 5-4 show unpublished calculations by Dr Timothy Gould of the phonon spectrum and density of states for PdH$_{\text{oct}}$ and PdH$_{\text{tetr}}$. The calculations were performed with VASP [4-7] and Phonopy [9].

Figure 5-3: Phonon band structures for Pd, PdH$_{\text{oct}}$ and PdH$_{\text{tetr}}$ for fixed lattice parameter $a = 4.0$ Å. Unpublished calculations by Dr. Timothy Gould.
Figure 5-4: Phonon densities of states for Pd, PdH\textsuperscript{oct} and PdH\textsuperscript{tet} for fixed lattice parameter \( a = 4.0 \ \text{Å} \). Unpublished calculations by Dr. Timothy Gould.

The effect of tetrahedral occupancy on the optical branches is strong, with very high frequency modes introduced. Recalling that \( \alpha(\omega) \) in the Eliashberg spectral function is small at low values of \( \omega \), the contribution of low-frequency phonon modes in Eqn (1.19) :

\[
\lambda \triangleq 2 \int_0^\infty \frac{1}{\omega} \alpha^2(\omega) F(\omega) d\omega,
\]

although it is scaled by \( 1/\omega \), is reduced by \( \alpha^2(\omega) \to 0 \) for small \( \omega \), and so the high-frequency modes may in fact contribute significantly to increasing \( \lambda \). Interestingly, tetrahedral occupancy does also shift the low-frequency modes down.
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Chapter 6, Conclusions and Perspectives

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Conclusions and Perspectives

6.1 Summary

High-temperature superconductivity has been found in the palladium–hydrogen and palladium–deuterium systems at 55–60 K after charging with hydrogen/deuterium at approximately 300 °C, cooling rapidly to about 40 K and measuring the resistivity while heating rapidly. The transition was not observed when the sample was cooled and heated slowly. A significant reverse isotope effect of approximately 5 K was found, just as was known in these systems at about 10 K following formation of the hydride at room temperature. The vanishing of the sample resistance within instrumental resolution, the existence of an isotope effect and the quenching of the superconducting transition by an applied magnetic field all indicate that superconductivity really was observed. A qualitative explanation based on occupancy of tetrahedral interstitial sites at 300 °C and frozen-in by rapid cooling was proposed and supported with calculations (by others) comparing the electron energies and phonon band structures.

6.2 Conclusions

The method developed for introducing and retaining hydrogen in the palladium host by loading at 300 °C and cooling to cryogenic temperatures as quickly as possible
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succeeded in revealing high-temperature superconductivity with $T_c \approx 55$ K for PdH$_x$ and
$\approx 60$ K for PdD$_x$ for $x \approx 1$. The increase in transition temperature for deuterium loading,
i.e. the inverse isotope effect, strongly suggests that the superconductivity is BCS-type,
i.e. established through the electron–phonon interaction, and strongly influenced by the
optical phonons associated with H/D vibrations.

Octahedral occupancy occurs when Pd is charged with D (and, it is assumed, H) at room temperature, but partial tetrahedral occupancy is likely at higher temperatures. The experimental results are consistent with the freezing-in of a high-temperature state which relaxes on a time scale of minutes at about 50 K to the equilibrium octahedral state. This metastable state could be the tetrahedral hydride.

The variability of the resistivity measured while heating the sample rapidly was not an instrumental problem, but was caused by variable electron scattering by phonons. This is most likely because the sample was highly inhomogeneous, consisting of normal regions of octahedral hydride mixed with superconducting regions of the metastable high-temperature state. The superconducting transition can be observed if there is a superconducting path across the sample, but not otherwise, which explains why the transition was not always observed. The higher rate of success in observing the superconducting transition after loading with deuterium is explained by the slower diffusion of D compared to H, so that the metastable deuteride superconducting state relaxed to the normal state more slowly.

The calculations by Dr Timothy Gould show that the speculated tetrahedral hydride is plausible. The electronic energies of PdH$_{tet}$ and PdH$_{oct}$ are similar enough that tetrahedral occupancy is likely at high temperatures, owing to thermal expansion of the lattice. The phonon band structures reveal the introduction of very-high frequency optical phonons in PdH$_{tet}$ because of the much stiffer H potential in the smaller
tetrahedral site. These modes may in fact contribute significantly to increase $\lambda$, in spite of the reciprocal weighting by frequency in calculating the moments of $\alpha^2(\omega)F(\omega)$. Interestingly, tetrahedral occupancy does also shift the low-frequency modes down. These considerations make high-temperature superconductivity based on tetrahedral occupancy plausible, although much more work is required to fully understand this fascinating discovery.

The high-temperature superconductivity discovered in this work occurs at the highest temperature for any BCS superconductor under relatively normal laboratory conditions. Only the very recent discovery of superconductivity in H$_2$S at up to 203 K under more than 100 GPa pressure exceeds this record. Although palladium hydride is the oldest, best known and most studied metal hydride, it still can surprise us with new phenomena.

6.3 **Future work**

The metastability of the high-temperature superconductivity in PdH/D needs to be controlled by improving the thermal response of the apparatus, so that the high-temperature state can be frozen-in at a low temperature (say 4 K) and studied with neutron diffraction. In-situ high-resolution diffraction should be done by loading deuterium into the palladium sample on the beam line, so that its effects on the crystallography of the sample can be measured directly, especially the interstitial occupancy. Deuterium is necessary because hydrogen is a very strong incoherent neutron scatterer, but D is advantageous anyway because it diffuses slower than H. Rietveld profile analysis can be used to analyse the data for the occupancies of $o$ and $t$ sites, whose sum is the total deuterium content.
Chapter 6. Conclusions and Perspectives

It is important to extend the laboratory-based experimental technique to simultaneously measure the magnetic as well as the electrical properties. The resistivity measurements reported here where performed in a vibrating-sample magnetometer that can measure resistance and magnetic moment simultaneously in He exchange gas, but not under high gas pressure. A modified sample environment which enables measurements under the desired temperature and pressure conditions is needed. If the picture of the superconducting hydride as a mixture of normal and superconducting regions is correct, the magnetic measurements will reveal a partial Meissner effect. This will allow the volume fraction of superconductor to be calculated.

When the hydrogen absorption takes place above the thermodynamical critical point (24 bar H$_2$/291 °C; 39 bar D$_2$/283 °C) no dislocations are formed, because the α and β phases merge. The hydride formed in the experiments reported here is dislocation-free, at least prior to quenching to low temperature. Whether this different metallurgical state has any influence on the superconductivity is unknown. It could be investigated by hydriding at room temperature, which creates dislocations owing to the different lattice parameters of the α and β phases, heating to 300 °C to form the high-temperature hydride, then following the usual procedure.

Adsorption-desorption isotherms at temperatures below 78 K have not been explored. Having these isotherms would be very helpful in understanding the hydride phases and to complement the neutron diffraction studies.

Theoretical modelling was beyond the scope of the project, but more work is needed to explain the experimental results. The most urgent need is for calculations of the various factors contributing to Eqn (1.26), following the methodology outlined in §1.4.3. A comparative theoretical study of PdH$_{tet}$ and PdH$_{oct}$ with calculations of $T_c$ would be very valuable.