SUPERCONDUCTIVITY IN Pd–Ag–H ALLOYS

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The tight binding coherent potential approximation is used to calculate the electron densities of states (DOS) for various concentrations of the Pd$_{1-y}$As$_y$H$_y$ system. The DOS are used in the evaluation of the electron–phonon coupling constant $\lambda$ and the superconducting transition temperature $T_c$. Our results reproduce the experimentally determined behavior of the superconducting transition temperature's dependency on Ag concentration, and provide a satisfactory explanation of the mechanism of superconductivity in this system.

1. Introduction

A good understanding of the mechanism of superconductivity in the palladium–hydrogen system has been obtained [1] using the results of band structure calculations, neutron scattering data and the theories of McMillan [2] and Gaspar and Gyorffy [3].

Ion-implantation experiments [4] in Pd$_{1-y}$As$_y$H$_y$ have shown that the superconducting transition temperature, $T_c$, increases by the addition of Ag in the range $0 < y < 0.3$, and rapidly decreases to zero for $y > 0.3$. The interpretation of these experiments has been more complicated than that of PdH due to lack of detailed information on the phonon spectra at the Ag-rich end and due to disorder effects on the electronic structure.

An attempt [5] to explain the variation of the superconducting temperature, $T_c$, in the Pd–Ag–H system led to the conclusion that, as in PdH, the hydrogen site s-like density of states at the Fermi level, $E_F$, is the controlling factor. However, in the quantitative sense these calculations predict $T_c$'s which are unrealistically high at the Ag-rich end. Since these calculations were based on the rigid band and virtual crystal approximation arguments it is reasonable to question their accuracy.

In the present work we have performed calculations of the density of states (DOS) and Pd$_{1-y}$As$_y$H$_y$ alloys using the tight binding coherent potential approximation (CPA) method [6]. These calculations have been used to evaluate the electron–phonon coupling and provide a satisfactory explanation of the $T_c$ variation in this system.

2. Calculation of the densities of states

We proceed by generating self-consistent augmented plane wave (APW) calculations for stoichiometric PdH and AgH and then obtaining highly accurate three-center orthogonal Slater-Koster [7] fits to the energy bands. The fit is done using 10 bands, i.e., s, p and d orbitals on the metal site and an s orbital on the hydrogen site. The CPA is then used to calculate the DOS for a given concentration, where no off-diagonal disorder is taken into account. We perform the Blalock zone averages on a uniform mesh of 505 $k$-points and we proceed in two steps. First we get an “effective metal” Pd$_{1-y}$As$_y$H$_{1.0}$ employing the CPA on the $9 \times 9$ metal submatrix which handles the disorder between Pd and Ag; and then using the results of the first step, we do another CPA calculation on the remaining hydrogen block of the matrix to treat the substitution of vacancies at hydrogen sites. Since our CPA neglects off-diagonal disorder, the off-diagonal
matrix elements of our effective Hamiltonian are averaged according to the concentrations.

Plots of our DOS results (decomposed by site and symmetry) for $y = 0.2$ and $x = 0.9$ are shown in figs. 1a and 1b, where we observe that the bands cannot be explained in a rigid band picture. Note that the d bands of Pd and Ag are distinct with the Pd band lying nearer the Fermi level.

If we keep the H concentration fixed and vary the Ag concentration, we can clearly observe the variation in intensity of the two separate d-band features—with the deeper band being enhanced with increasing $y$ at the expense of the higher lying Pd d-band.

3. Calculation of $T_c$

In order to calculate the $T_c$ we employ the Allen Dynes [8] modification to the McMillan equations:

$$
T_c = \frac{\omega_{\text{p}}}{1.20} \exp \left[ - \frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right],
$$

(1)
where $\lambda$ is the electron–phonon coupling constant, $\mu^*$ is the Coulomb pseudopotential given by the Bennemann–Garland [9] formula:

$$\mu^* = 0.26N(E_{f})/[1 + N(E_{f})].$$

To calculate $\lambda$ we write

$$\lambda = \frac{\eta_H}{M_H \langle \omega^2(y) \rangle_H} + \frac{\eta_{\text{met}}}{M_{\text{met}} \langle \omega^2(y) \rangle_{\text{met}}}$$

$$\lambda = \lambda_H + \lambda_{\text{met}},$$

(2)

where $\eta_H$ and $\eta_{\text{met}}$ are the electronic part of the electron–phonon interaction which depends solely on band structure quantities.

$$\lambda_{\text{met}} = \lambda_{\text{Pd}} + \lambda_{\text{Ag}},$$

$$\lambda_{\text{met}} = \frac{\eta_{\text{Pd}} + \eta_{\text{Ag}}}{M_{\text{met}} \langle \omega^2(y) \rangle_{\text{met}}},$$

(3)

where

$$M_{\text{met}} \langle \omega^2(y) \rangle_{\text{met}} = y M_{\text{Ag}} \langle \omega^2 \rangle_{\text{Ag}} + (1 - y) M_{\text{Pd}} \langle \omega^2 \rangle_{\text{Pd}}$$

(4)
and
\[ M_{H} \langle \omega^2(y) \rangle_{H} = (1 + y) M_{H} \langle \omega^2 \rangle_{H} \bigg|_{y=0}. \]  (5)

The phenomenological eq. (5) is designed to increase the hydrogen site \( M \omega^2 \) in a manner consistent with the experimental information [10] that \( \lambda_{H}/\lambda_{\text{met}} = 0.8 \) in AgD to be compared [1] with the value of 2.6 in PdD. In eq. (4) \( \omega_{\text{Ag}} \) is derived from the available neutron scattering data for PdH and the corresponding Debye temperatures of pure Pd and Ag.

To implement the scheme outlined above we must obtain the \( \eta \) for each constituent of the alloy at every concentration. In a stoichiometric alloy this is done by the theory of Gaspari and Gyorffy [3] which requires knowledge of the scattering phase shifts in addition to the partial DOS at \( E_{\text{F}} \).

In the tight binding CPA formalism phase shifts cannot be calculated; but they have a weak dependence on the small variation of \( E_{\text{F}} \). Thus we have assumed them to be constant and we have postulated that [6]:
\[ \eta^{\alpha} = C^{\alpha} n^{\alpha}(E_{\text{F}}), \]  (6)

where \( \alpha \) represents the constituent (Pd, Ag or H).

For Pd and H we proceed in the following manner: Using known values [1] for \( \eta^{\text{Pd}(H)} \) and \( n^{\text{Pd}(H)}(E_{\text{F}}) \) for the stoichiometric case, PdH, we obtain \( C^{\text{Pd}} \) and \( C^{\text{H}} \). These are then used at each concentration to find \( \eta^{\text{Pd}} \) and \( \eta^{\text{H}} \) employing eq. (6).

To obtain \( C^{\text{Ag}} \), which is unreliable if we employ AgH because of the very small value of \( \eta \) at that limit, we make use of the experimental finding [10] that \( \lambda_{H}/\lambda_{\text{met}} \approx 0.8 \) for AgD, which is deuterium-rich. This is used with results of Ag(90)Pd(10)H(99) as described below.

For a given \( y \) and \( x \), \( \lambda_{H} \) can be calculated and thus using the previous relationship (for \( y > 0.9 \)), \( \lambda_{\text{met}} \) can also be determined. Then using eq. (3), we get
\[ \eta^{\text{Ag}} = \lambda_{\text{met}} [M_{\text{met}} \langle \omega^2 \rangle_{\text{met}}], y \rangle - \eta^{\text{Pd}} \]  (7)

which in conjunction with eq. (5) yields \( \eta^{\text{Ag}} \). Finally, \( C^{\text{Ag}} \) is determined from eq. (6). This guarantees qualitative agreement of the calculation with the experiment (for the ratio \( \lambda_{H}/\lambda_{\text{met}} \)) in the Ag-rich end.

4. Discussion

We present the calculation of \( T_{\text{c}} \) as a function of silver concentration (0 \( \leq y \leq 0.9 \)) for a fixed concentration of H (\( x = 0.99 \)).

In fig. 2 we compare \( T_{\text{c}} \) obtained from this calculation with data obtained from experiments [4] on Pd_{1-y}Ag_yH_x systems of high (but not precisely determined) hydrogen content. The qualitative behavior of \( T_{\text{c}} \) — i.e., initially rising with the addition of Ag until some maximum value after which it declines sharply is well reproduced, although the details (position and value of the maximum) do not coincide.

This particular variation of \( T_{\text{c}} \) with Ag concentration can be understood if we consider the various factors which enter into the calculation.

In fig. 3 we present \( \lambda_{H} \) and \( \lambda_{\text{met}} \) vs. \( y \). In comparing figs. 2 and 3 we observe that \( T_{\text{c}} \) follows \( \lambda_{H} \), with \( \lambda_{\text{met}} \) playing only a secondary role. That is, the metal contributions affect the final value of \( T_{\text{c}} \), but the trend is determined by the dominant H term.

A further understanding of the mechanism of superconductivity in this system can be obtained by inspection of fig. 4, which gives \( \eta \) vs. at% Ag for both hydrogen and metal. The quantity \( \eta \),

![Fig. 2. Superconducting temperature, Tc, plotted against Ag concentration.](image-url)
which depends on electronic structure only, shows similar behavior as a function of \( y \) as that seen in fig. 2 for \( T_c \). However, here the peak in \( \eta_H \) does not occur at the same region of \( y \) as in the experimentally determined \( T_c \). Thus a calculation of \( T_c \) which does not take into account the variation of the phonon spectra, and thus \( M(\omega^2) \), with the Ag concentration yields a \( T_c \) vs. \( y \) curve which has a maximum at an unrealistically high Ag concentration.

In contrast to this we see fig. 3 where \( \lambda \), the electron–phonon coupling term, has been calculated taking into account a variation of \( M(\omega^2) \) with Ag concentration. This variation in \( M(\omega^2) \) shifts the maximum to smaller \( y \) enabling us to reproduce the variation of \( T_c \) reasonably well.

**References**


