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SUPERCONDUCTIVITY IN PALLADIUM BASED HYBRIDES

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Abstract.- Calculations of the superconducting properties of Pd-based hydrides are presented. The results are in very good agreement with experiment for PdH, PdD, Pd-Rh-H and for low Ag concentration in Pd-Ag-H.

We have calculated the electron-phonon coupling constant $\lambda$ and the superconducting transition temperature $T_c$ of systems PdH$_x$, PdD$_x$Pd$_{1-y}$Ag$_y$H$_x$ and Pd$_{1-y}$Rh$_y$H$_x$. These calculations were based on first principles augmented plane wave (APW) calculations, from which the density of electronic states (DOS) as well as the site and angular momentum decomposed partial DOS were obtained. The Fermi level values of the DOS's and the scattering phase shifts were used in an extension /1/ of the Gaspari and Gyorffy /2/ theory to calculate the electron-phonon spectral function $\gamma$ and $\lambda$ utilizing also neutron scattering measurements /3,4/.

The critical $T_c$ was found from the equation proposed by Dynes /5/, which is adequate for calculating $T_c$ to within the accuracy of band calculations.

We have used the methodology described above, namely band structure calculations, measured phonon spectra and the value of the Coulomb pseudo-potential $\mu$ obtained from the Bennemann and Garland /6/ formula, to calculate $T_c$ for PdH(D). Details of these calculations have been presented elsewhere /7,8/. We now summarize these results. We note that although no adjustable parameters were used an $T_c$ is a very sensitive function of $\lambda$, the calculated values are in very good agreement with the measurements /9/.

The results show that the high value of $T_c$ is mainly due to the optic phonon mode associated with local hydrogen vibration, thus verifying quantitatively an earlier suggestion by Ganguly /10/. Ganguly /10/ has also proposed that the observed isotope effect /9/ is due to an enhancement of the optic mode in PdH relative to the harmonic value as a result of anharmonic effects. Rahman at al. /4/ have found, by analyzing their neutron scattering measurements on PdH$_{0.63}$ and comparing them with the PdH$_{0.63}$ data /3/, the following relationship between the force constants : $K_{Pd-H}^{1.2} < K_{Pd-D}$. Using this result we have obtained /7,8/ quantitative agreement with the measured values of $T_c$ for PdD and PdH, thus confirming Ganguly's explanation.

We have also calculated the $x$-dependence of $T_c$ for PdH$_x$ and PdD$_x$ /7,8/. In this calculations we employed the rigid band model, which allowed us to use the band structure of the stoichiometric case ($x=1.0$). We have presented /8/ convincing arguments as to why the rigid band is a good approximation for calculating $\lambda$ in the range $0.75<x<1.0$. The results of these calculations, with no adjustable parameters, were in impressive agreement with experiment. The physical picture which emerged for the $x$-dependence of $T_c$, is that the strong hydrogen dependence is due to a change with $x$ in the nature of electronic eigenstates at the Fermi level $E_F$. As $x$ increases the $s$-character of the H(D) site DOS increases. This means that the electrons at $E_F$ have higher probability to be found around the H(D) sites and consequently to couple with the relatively soft H(D) "local" mode. The validity of this picture has been verified by our coherent potential approximation (CPA) calculations /11/ for substoichiometric PdH$_x$. These calculations were performed using a tight binding form of the CPA /12/, based on a more sophisticated Slater-Koster Hamiltonian than that used in reference /12/. The
Slater-Koster fit to the APW results was done in the NaCl structure without making the two-center approximation and involved 38 interaction integrals as parameters.

The fact that our PdH rigid band and CPA results are in good agreement with each other for states around the Fermi level, encouraged us to proceed to a study of Pd$_{1-y}$Rh$_y$H$_x$ and Pd$_{1-y}$Ag$_y$H$_x$ in the following manner. We have calculated the band structure of these materials by making the virtual crystal approximation (VCA) to treat the $y \neq 0.1$ cases. According to the VCA we have assumed that the NaCl structure is maintained, and obtained crystal potentials for the APW calculations of the alloy cases by averaging the potentials of PdH$_{1.0}$ with RhH$_{1.0}$ and of PdH$_{1.0}$ with AgH$_{1.0}$. To handle the $x \neq 1$ cases we have used the rigid band approximation. These calculations were done with the lattice constant of PdH$_{1.0}$, which is a reasonable assumption for $x > 0.5$, according to the measurements of Axelrod and Makrides /13/.

To obtain the quantity $\eta$ we have applied the theory of Gaspari and Gyorffy /2/. As discussed previously /1/ we calculate $\eta_{H}$ which corresponds to the optic mode and $\eta_{Pd(Rh,Ag)}$ which corresponds to the acoustic mode. We have found that $\eta_{Pd(Ag)}$ is small and almost independent of $x$. The important parameter, in determining superconductivity in these systems, is $\eta_{H}$. Figure 1 shows $\eta_{H}$ versus hydrogen concentration for the different alloys considered. We note from this figure that the addition of Rh to PdH decreases the electron-phonon interaction $\eta_{H}$, while the addition of Ag to PdH increases $H$.

The objective is to estimate $T_{c}$ rather than merely $\eta$. To do this we need to know $\lambda$, the coupling constant, which means we must have data on the phonon spectra. Such data are available /14/ only for Pd$_{1-y}$Ag$_y$H$_x$ up to $x \leq 0.2$ or 0.3. The data show that alloying PdH with small amounts of Ag does not alter the optic-mode frequency, $\omega_{opt}$, significantly. If we assume that $\omega_{opt}$ has a constant value for alloys of Pd with either Rh or Ag, then $T_{c}$ decreases monotonically with additions of Rh and increases monotonically with additions of Ag because of the change in $\eta_{H}$ shown in figure 1. These estimated values of $T_{c}$ agree with experiment for all values of Rh but only up to 0.3 Ag. To bring calculated and measured $T_{c}$ into agreement for greater additions of Ag it is necessary to assume that $\omega_{opt}$ increases with increasing Ag content.

![Figure 1: Electron-phonon interaction $\eta_{H}$ plotted as a function of hydrogen concentration $x$.](image-url)

Such a variation in $\omega_{opt}$ would also have salubrious effects in matching the calculated maximum in $T_{c}$ versus $x$ to experimental values.

**References**


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