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SUPERCONDUCTIVITY IN PALLADIUM BASED HYBRIDES

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Résumé.— On présente les calculs des propriétés supraconductrices de composés hydrogénés à base de Palladium. Les résultats s'accordent bien avec l'expérience pour PdH, PdD, Pd-Rh-H et pour Pd-Ag-H. à faible concentration d'Argent.

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 λ and the superconducting transition temperature T_c of systems PdH_x , PdD_x , $\text{Pd}_{1-y}\text{Ag}_y\text{H}_x$ and $\text{Pd}_{1-y}\text{Rh}_y\text{H}_x$. 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 η and λ 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 μ^* 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 T_c is a very sensitive function of λ , 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 inverse

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 et al. /4/ have found, by analyzing their neutron scattering measurements on $\text{PdH}_{0.63}$ and comparing them with the $\text{PdD}_{0.63}$ data /3/, the following relationship between the force constants: $K_{\text{Pd-H}} \approx 1.2 K_{\text{Pd-D}}$

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 these 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 λ in the range $0.75 < x \leq 1.0$. 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

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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 $\text{Pd}_{1-y}\text{Rh}_y\text{H}_x$ and $\text{Pd}_{1-y}\text{Ag}_y\text{H}_x$ 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 $\text{PdH}_{1.0}$ with $\text{RhH}_{1.0}$ and of $\text{PdH}_{1.0}$ with $\text{AgH}_{1.0}$. To handle the $x \neq 1$ cases we have used the rigid band approximation. These calculations were done with the lattice constant of $\text{PdH}_{1.0}$, which is a reasonable assumption for $x > 0.5$, according to the measurements of Axelrod and Makrides /13/.

To obtain the quantity η we have applied the theory of Gaspari and Gyorffy /2/. As discussed previously /1/ we calculate η_H which corresponds to the optic mode and $\eta_{\text{Pd(Rh,Ag)}}$ which corresponds to the acoustic mode. We have found that $\eta_{\text{Pd(Ag)}}$ is small and almost independent of x . The important parameter, in determining superconductivity in these systems, is η_H . Figure 1 shows η_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 η_H , while the addition of Ag to PdH increases η_H .

The objective is to estimate T_c rather than merely η . To do this we need to know λ , the coupling constant, which means we must have data on the phonon spectra. Such data are available /14/ only for $\text{Pd}_{1-y}\text{Ag}_y\text{H}_x$ up to $y \approx 0.2$ or 0.3 . The data show that alloying PdH with small amounts of Ag does not alter the optic-mode frequency, ω_{opt} , significantly. If we assume that ω_{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 η_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 ω_{opt} increases with increasing Ag content.

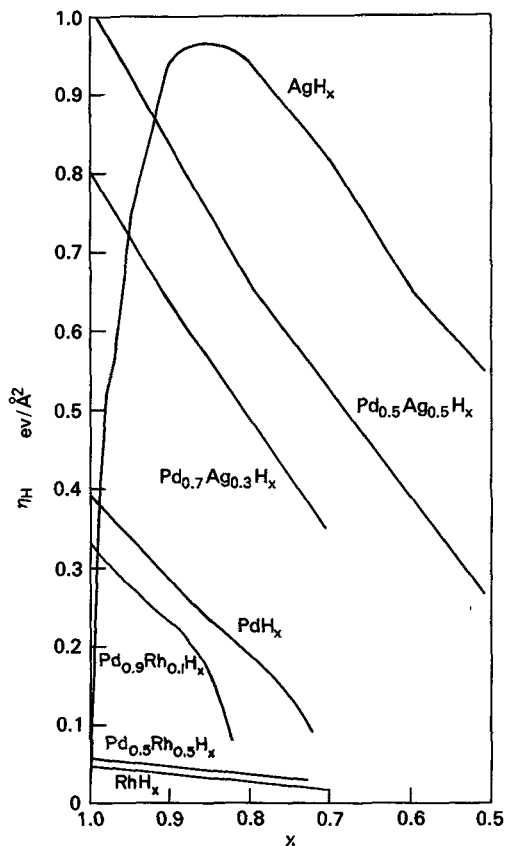


Fig. 1 : Electron-phonon interaction η_H plotted as a function of hydrogen concentration x .

Such a variation in ω_{opt} would also have salubrious effects in matching the calculated maximum in T_c versus x to experimental values.

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