

PLATINUM HYDRIDE: A POSSIBLE HIGH TEMPERATURE SUPERCONDUCTOR*

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Summary

Calculations of the band structure of PtH suggest an electronic properties picture almost identical with that of PdH. Evaluation of the electron-phonon interaction from the densities of states and phase shifts resulting from the band structure calculations also yields a striking similarity between PtH and PdH. On the basis of these results and the assumption that the phonon spectra of PtH and PdH are also similar, the possibility of PtH being a high temperature superconductor is explored.

1. Introduction

In a series of recent papers [1 - 5] we have presented calculations of the superconducting properties of the Pd-H system. These studies have led us to the following conclusions. (1) The appearance of superconductivity in the palladium-based hydrides is mainly caused by soft-optic-mode phonon frequencies which are associated with local hydrogen vibrations. (2) The dependence of the transition temperature T_c on the hydrogen and noble metal concentrations is mainly controlled by the Fermi level value of the hydrogen s-like density of electronic states. (3) The inverse isotope effect is caused by an increase of the Pd-H force constant over the Pd-D force constant because of enhanced anharmonicity of the hydrogen motion.

In this paper we would like to speculate on the possibility that platinum hydride also has a high superconducting transition temperature T_c . To examine this we performed a band structure calculation for PtH, using the same techniques as in our PdH work. Although no crystalline PtH has been reported in the literature we assume that hydrogen may be introduced in the platinum lattice, at least by ion implantation.

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2. Results and discussion

The band structure calculation was performed by the spin-independent relativistic augmented plane wave (APW) method, assuming the NaCl crystal structure and a lattice constant a_0 of 7.78 a.u. This value of a_0 was found by increasing the lattice spacing of pure platinum by the same percentage that the a_0 value of PdH increases over the a_0 of palladium. The muffin-tin sphere radii ($R_{\text{Pt}} = 2.395$ a.u. and $R_{\text{H}} = 1.495$ a.u.) were kept in the same proportion as that used in our PdH work [3]. The exchange potentials were determined using the $X\alpha$ parameters 0.693 and 0.777 for platinum and hydrogen respectively [6]. In our PdH work [3] we have shown that there is no qualitative difference between our self-consistent (SC) and non-self-consistent calculations, especially in the region around the Fermi level. Because of this we find it sufficiently accurate to base the present study on a non-self-consistent band structure calculation.

The APW calculation was carried out on a mesh of 89 k points in 1/48th of the Brillouin zone. The energy eigenvalues and the electronic charges inside the muffin-tin spheres were interpolated using the tetrahedron method [7] to obtain the total density of states (DOS) and the angular momentum components per site inside the muffin-tin spheres. The DOS results are shown in Fig. 1; it should be noted that there is a very close resemblance to the DOS of PdH [3]. This similarity between PtH and PdH is expected since platinum and palladium have the same number of valence electrons and there is very little difference in the lattice constants. It should also be noted that, as in PdH, the total DOS and the dominant d-like component decrease as the Fermi level E_{F} is approached in the energy range from 0.65 rydberg to E_{F} . However, the s- and p-like DOS increase in this energy region. In our PdH work [2, 3] we have concluded that the increase of the s-like hydrogen DOS is responsible for the enhancement of T_{c} . This also seems to apply to PtH provided that soft-optic-mode frequencies similar to those of PdH can be assumed. It should be mentioned that the large value of the hydrogen DOS shown for low energies is dependent on the choice of the muffin-tin sphere radii and therefore cannot be used for any quantitative comparison of the DOS for the two sites.

In the present work the rigid-band approximation was made in order to evaluate the total and decomposed DOS and the scattering phase shifts δ_1 as a function of energy. It should be emphasized that the rigid-band approximation is applied to an energy range $\Delta E = 0.05$ rydberg just below E_{F} . As can be seen from Fig. 1, this energy range is above the last peak of the platinum d-band complex and corresponds to smooth DOS functions.

These values of the DOS and δ_1 were used in the theory of Gaspari and Gyorffy [8] to calculate the electron-phonon interactions η_{H} and η_{Pt} for the hydrogen and platinum sites of PtH. The results of this calculation are given in Table 1. The values of η_{H} and η_{Pt} are significantly higher than the corresponding values that we have reported from our SC band structure calculations of PdH [3]. However, for PdH we had found that the η values

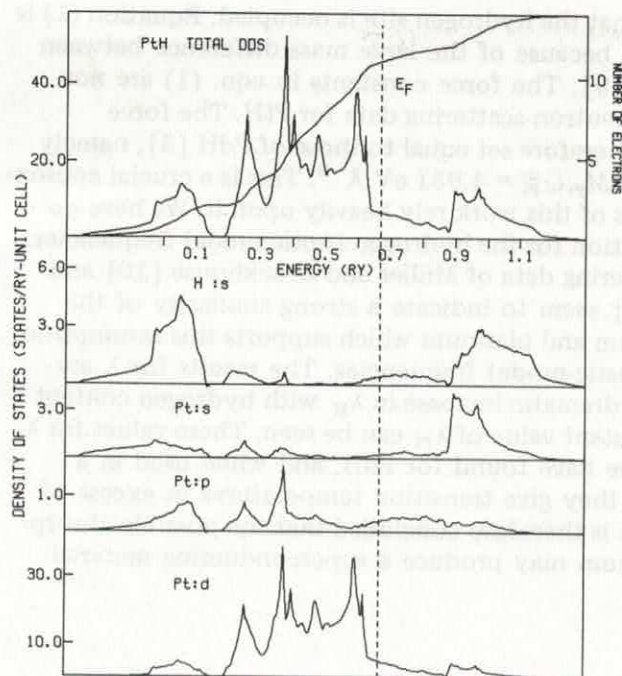


Fig. 1. The total and decomposed DOS for PtH. It should be noted that the decomposed DOS are given within the muffin-tin sphere volume.

TABLE 1

Electron-phonon interactions η_{H} and η_{Pt} as functions of hydrogen content x for PtH

x	$x\eta_{\text{H}}$ (eV \AA^{-2})	η_{Pt} (eV \AA^{-2})
1.00	0.50	1.41
0.95	0.45	1.39
0.90	0.45	1.43
0.85	0.35	1.33
0.80	0.28	1.20
0.75	0.17	1.30
0.70	0.09	1.31
0.65	0.07	1.41
0.60	0.05	1.49

computed from the non-self-consistent calculations were higher than those computed from the SC calculation. Thus, if we performed an SC calculation for PtH, we would expect η to be less but still sufficiently large to allow the prediction discussed in this paper. These values were then used to determine the electron-phonon coupling constant λ from the following expression:

$$\lambda(x) = \frac{x\eta_{\text{H}}(x)}{M_{\text{H}}\bar{\omega}_{\text{H}}^2} + \frac{\eta_{\text{Pt}}(x)}{M_{\text{Pt}}\bar{\omega}_{\text{Pt}}^2} \quad (1)$$

where x is the probability that the hydrogen site is occupied. Equation (1) is a good approximation to λ because of the large mass difference between hydrogen and platinum [3, 9]. The force constants in eqn. (1) are not known since there are no neutron-scattering data for PtH. The force constants in eqn. (1) were therefore set equal to those of PdH [3], namely $M_{\text{H}}\bar{\omega}_{\text{H}}^2 = 1.062 \text{ eV \AA}^{-2}$ and $M_{\text{Pt}}\bar{\omega}_{\text{Pt}}^2 = 4.951 \text{ eV \AA}^{-2}$. This is a crucial approximation and the conclusions of this work rely heavily upon it. We have no way to support this assumption for the hydrogen (optic-mode) frequencies. However, the neutron-scattering data of Müller and Brockhouse [10] and those of Dutton *et al.* [11] seem to indicate a strong similarity of the phonon spectra for palladium and platinum which supports this assumption for the platinum site (acoustic-mode) frequencies. The results for λ are plotted in Fig. 2 where the dramatic increase in λ_{H} with hydrogen content and the approximately constant value of λ_{Pt} can be seen. These values for λ are close to the λ values we have found for PdH, and when used in a McMillan-like T_c equation they give transition temperatures in excess of 10 K near stoichiometry. It is therefore concluded that the possible absorption of hydrogen by platinum may produce a superconducting material similar to PdH.

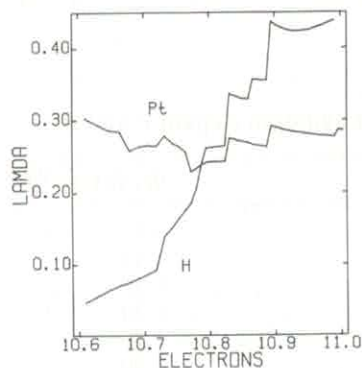


Fig. 2. Electron-phonon coupling constants λ_{H} and λ_{Pt} plotted as functions of the number of conduction electrons. 11 electrons correspond to full stoichiometry $x = 1.0$. The jaggedness of these graphs is not physical; it simply reflects the computational uncertainty of the calculation.

Acknowledgments

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References

- 1 D. A. Papaconstantopoulos and B. M. Klein, *Phys. Rev. Lett.*, **35** (1975) 110.
- 2 B. M. Klein, E. N. Economou and D. A. Papaconstantopoulos, *Phys. Rev. Lett.*, **39** (1977) 574.
- 3 D. A. Papaconstantopoulos, B. M. Klein, E. N. Economou and L. L. Boyer, *Phys. Rev. B*, **17** (1978) 141.
- 4 D. A. Papaconstantopoulos, B. M. Klein, J. S. Faulkner and L. L. Boyer, *Phys. Rev. B*, **18** (1978) 2784.
- 5 D. A. Papaconstantopoulos, E. N. Economou, B. M. Klein and L. L. Boyer, *Phys. Rev. B*, **20** (1979) 177.
- 6 K. Schwarz, *Theor. Chim. Acta*, **34** (1974) 255.
J. C. Slater, *Int. J. Quantum Chem.*, **S7** (1973) 533.
- 7 G. Lehmann and M. Taut, *Phys. Status Solidi B*, **54** (1972) 469.
- 8 G. D. Gaspari and B. L. Gyorffy, *Phys. Rev. Lett.*, **28** (1972) 801.
- 9 B. M. Klein and D. A. Papaconstantopoulos, *J. Phys. F*, **6** (1976) 1135.
- 10 A. P. Miiller and B. N. Brockhouse, *Can. J. Phys.*, **49** (1971) 704.
- 11 D. H. Dutton, B. N. Brockhouse and A. P. Miiller, *Can. J. Phys.*, **50** (1972) 2915.

