the instability region has a length l and the plasma moves through this region at the expansion velocity W, one has an increase of the ion temperature $\Delta T_i \sim (m/M)^{1/2}\omega_{pi}(I/Nc)l/W$. Assume that $l \sim 10\ \mu\text{m}$, $W \sim c_s \sim 3\times10^7$ cm sec^{-1}; then for $I = 10^{14}$ W/cm^2 we have $\Delta T_i \sim 1$ keV the total number of neutrons is $\frac{1}{2}N^2\langle\sigma V_r\rangle(l/W)\pi r^2 c_s \tau$, where r is the radius of the focal spot, V_r the relative speed, σ the ion cross section, τ the duration of the laser pulse, and the brackets indicate the average over the distribution function that I take as Maxwellian. In Bobin's experiments, the duration was 3×10^{-9} sec. Hence, for the $d(dn)$ reaction channel, $\langle\sigma V_r\rangle \sim 8\times10^{-23}$ cm^3 sec^{-1} at $T_i \sim 1$ keV. If $r \sim 100\ \mu\text{m}$ and $c_s \sim W$, we get a neutron yield of 10^4. This is the order of magnitude observed.[1] On the other hand, for $r \sim 50\ \mu\text{m}$ and a duration of 30 psec, if we assume for laser target interaction that the ion temperature saturates at 10 keV, we have $\langle\sigma V_r\rangle \sim 6\times10^{-19}$ cm^3 sec^{-1} and the neutron yield is about 3×10^5.

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Electronic Model for the Reverse Isotope Effect in Superconducting Pd-H(D)†

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The large reverse isotope effect in the Pd-H(D) system is confirmed over a range of composition in samples prepared by cathodic charging. It is shown that by shifting the T_c-versus-composition curve for the deuteride by about 0.05 in atomic ratio it can be made to coincide with the data for the hydride. A qualitative explanation is given in terms of proposed differences between the hydride and the deuteride in electronic structure.

Skoskiewicz[1] first observed that PdH$_x$ was superconducting for $x \approx 0.8$ and that T_c increased steeply with increasing H concentration. Stritzker and Buckel,[2] using ion implantation at low temperatures to extend the range of concentration of both the hydride and the deuteride beyond the equilibrium values at room temperature, found maxima in T_c of 11 and 9 K, respectively, for the deuteride and the hydride—a large reverse isotope effect—at compositions estimated to be about H(D)/Pd = 1.0. Since their method did not permit precise determination of the H or D concentrations in their samples, we considered it worthwhile to test their results in samples in which the concentrations could be measured.

We used a method of electrolytic charging at − 78°C, similar to that reported by Harper, Hammond, and Geballe,[3] to prepare samples with which to investigate the concentration dependence of the transition temperature and the reverse isotope effect in Pd-H and Pd-D. Our samples were 25-mm by 3-mm rectangles of 50-μm Pd foil, charged in an electrolyte solution of one part 38% HCl (DCl) in H$_2$O (D$_2$O) to nine parts CH$_3$OH

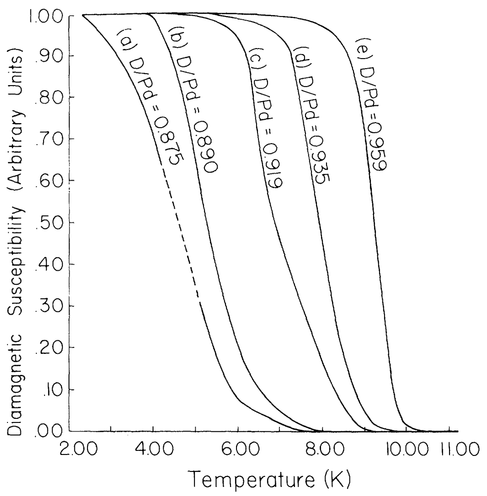

FIG. 1. Transition curves for samples of Pd-D. Transitions for Pd-H samples were similar in breadth but lower in temperature.

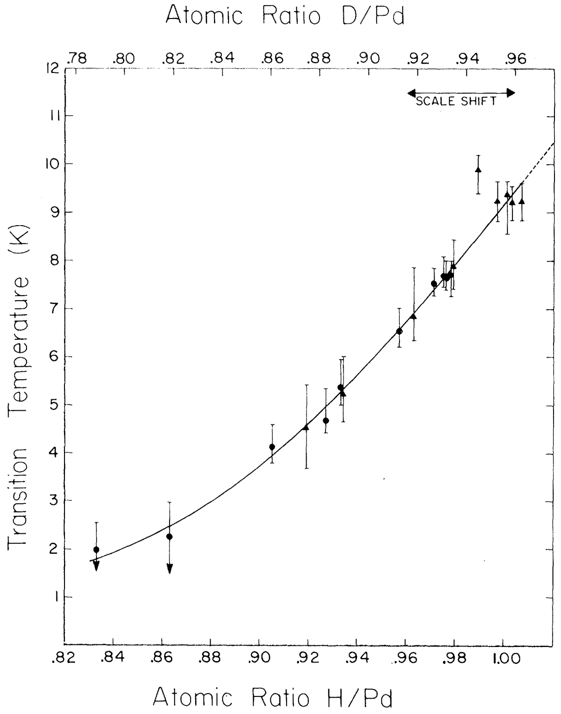

FIG. 2. Transition temperature of samples of Pd-H (●) and Pd-D (▲) versus atomic ratio (H/Pd, lower scale; D/Pd, upper scale). Shift of atomic ratio scales is 0.044 and bars indicate points of 80% and 20% of maximum diamagnetism.

(CH_3OD) with use of a Pt anode. The electrolytic cell was cooled to − 78°C with dry ice and acetone and was blanketed with dry N_2 to prevent contamination with atmospheric moisture. Concentrations of H (D) were varied by varying the charging period from 8 min to 3 h and were determined by thermal decomposition, measuring volumetrically the H (D) evolved. Values of atomic ratio are believed to be accurate to about 1%. Transition curves were determined by an ac measurement of the magnetic susceptibility at 200 Hz.

Representative curves of diamagnetic susceptibility versus temperature are shown in Fig. 1 for samples of Pd-D. The nature of the transition in Pd-H samples was comparable. We show in Fig. 2 that the curves of transition temperature versus composition for Pd-H and Pd-D can be made to coincide quite closely by shifting the Pd-D curve approximately 0.05 (actually 0.044) in atomic ratio on the composition axis. This suggests that for those qualities which are responsible for superconductivity, the deuteride at composition PdD_x is equivalent to the hydride at composition $PdH_{x+\delta}$, where δ is about 0.05. Recent results of Schirber and Northrup[4] on T_c versus atomic ratio in Pd-H(D) samples prepared by high-pressure synthesis are in reasonable agreement with our results.

We attribute this shift to a difference in *electronic structure* between the two systems and propose that the difference arises from the inequality in the zero-point motion between the hydrogen and the deuterium, and that anomalous isotope effects in other properties of the Pd-H(D) system may also be explainable in terms of this difference in electronic structure.

The electronic structure of the Pd-H system deviates appreciably from the rigid-band model earlier thought to be adequate; nonetheless, the electronic structure of Pd provides a framework for understanding the structure of Pd-H(D).

The Fermi level in Pd lies near the top of the $4d$ bands, leaving 0.36 unfilled d state per Pd atom, and it also intersects the broad $5sp$ bands, as determined by Fermi-surface studies[5,6] and verified by band-structure calculations.[7]

Switendick and co-workers[8,9] have performed energy-band calculations for PdH (and also for Pd_4H and Pd_4H_3 simulating the unsaturated PdH_x). They find, in addition to the $4d$ bands and the $5sp$ bands of Pd, states which are lowered and hybridized with the hydrogen s states, forming a group of levels which are centered about 5 to 6 eV below the Fermi level and which are H-Pd bonding states. Evidence that these low-lying H-induced states exist is found in the photoemission experiments of Eastman, Cashion, and Switendick.[9]

This significant alteration in the band structure results in electrons from the added hydrogen atoms filling three distinct types of states: (1) the H-induced bonding states, the number depending upon H/Pd and approaching 0.5 electron state per Pd at H/Pd = 1; (2) the 0.36 hole in the *d* bands of Pd; and finally, (3) the *sp* bands of Pd extending above the top of the *d* bands.

The first two kinds fill without appreciably increasing the Fermi energy, and so are filled easily. With increasing hydrogen concentration, the filling of these states should be signaled by the vanishing of paramagnetism and an abrupt leveling off of the electronic specific-heat coefficient, both of which have been observed experimentally.[10,11] Further uptake of hydrogen involves filling of the *sp* bands which is energetically less favorable because the low density of states in these bands requires a significant increase in energy per electron added.

The bonding states are present in both the hydride and the deuteride and the photoemission studies[9] indicate that they are at approximately the same energy. We propose, however, that the degree of bonding in the deuteride is significantly less than in the hydride because the number of electrons in the bonding states is less. Maeland and Flanagan[12] have determined the lattice constants for the hydride and the deuteride at comparable concentrations and find values of 4.027 Å for D/Pd = 0.56 compared with 4.025 Å for H/Pd = 0.58. A larger lattice constant for the deuteride than for the hydride is a surprising result since the hydrogen atom will certainly occupy a larger volume with its larger zero-point amplitude. The only reasonable explanation is that the binding forces in the hydride are larger than in the deuteride.

Magnetic-susceptibility results also suggest a difference in binding. From the data of Jamieson and Manchester,[13] it appears that the paramagnetism vanishes at D/Pd ≅ 0.56 and at H/Pd ≅ 0.62; see Fig. 3. Since the *d* bands can be assumed to be rigid enough to be essentially unaffected by the exchange of D for H, this indicates that about 0.05 more electron per Pd atom is involved in the bonding states in the hydride than in the deuteride.

The fundamental difference between the hydride and the deuteride is the mass of the hydrogen isotope, with consequent differences in the energy and amplitude of its zero-point motion,[14] and we believe that this is responsible for the difference in binding.

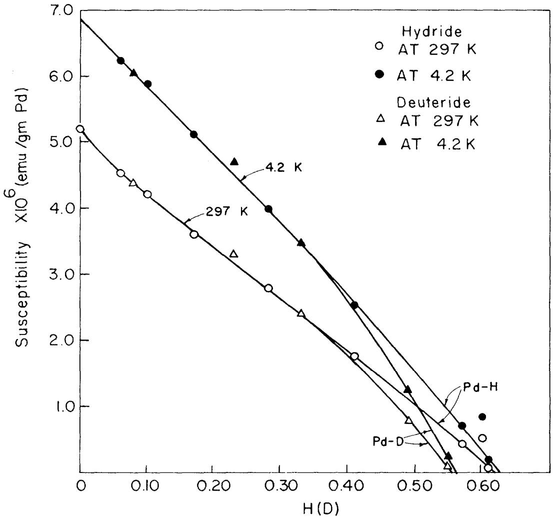

FIG. 3. Magnetic susceptibility of Pd-H and Pd-D versus atomic ratio, H(D)/Pd, at 4.2 and 297 K from Ref. 12. (Smoothed curves are ours.)

The root-mean-square displacement, u_{rms}, of H atoms from their equilibrium positions in samples of PdH_x has been determined from neutron scattering, and in one study,[15] u_{rms} for the hydride is compared with that for the deuteride: $u_{\mathrm{rms}}(\mathrm{H}) = 0.23$ Å in $\mathrm{PdH}_{0.706}$ and $u_{\mathrm{rms}}(\mathrm{D}) = 0.20$ Å in $\mathrm{PdD}_{0.658}$ at room temperature. Since the lattice constants are comparable for the hydride and the deuteride, the hydrogen, on time average, would be in closer proximity to the surrounding Pd atoms than would the deuterium. Therefore, the overlap of wave functions with those of Pd atoms would be greater for the hydrogen than for the deuterium and the hybridized Pd-H bonds should involve more electron states than the Pd-D bonds.

Superconductivity in this system appears to be critically dependent upon the extent to which the *sp* bands are filled above the top of the *d* bands, since T_c rises steeply with addition of hydrogen at concentrations above $\mathrm{PdH}_{0.7}$. Under the assumption that approximately 0.05 more electron per Pd atom is involved in bonding in the hydride than in the deuteride, equivalent filling of the *sp* bands would occur at a higher concentration in the hydride than in the deuteride, and equivalent T_c's would be found for $\mathrm{PdH}_{x+\delta}$ and PdD_x, where δ is the order of 0.05, accounting for the observed isotope effect.

The negative pressure coefficient of T_c, $dT_c/dp \approx -30$ mK/kbar,[16] is also consistent with our model. As the lattice constant is decreased with increasing pressure, H-Pd bonding would be enhanced, involving more electrons in bonding states, thus leaving fewer electrons in the *sp* bands, resulting in lower T_c. This model neither necessitates nor excludes the involvement of the optical H (D) modes in the superconducting pairing interaction. It only indicates that if they are involved, the coupling is essentially independent of frequency in going from the hydride to the deuteride, consistent with the predictions of the McMillan strong-coupling theory.[17]

It should be noted that two studies of the Pd-Ag-H(D) system, viewed together, cast doubt that the H (D) local modes are responsible for the isotope effect. Neutron scattering experiments of Chowdhury and Ross[18] on this system indicate that the local modes are not appreciably altered by alloying with Ag, yet Buckel and Stritzker[19] find that the isotope effect evident in Pd-H(D) gradually disappears with increasing percentages of Ag in the Pd-Ag-H(D) system.

Other attempts to explain the reverse isotope effect have been based on differences in phonon properties between the hydride and the deuteride.[20,21] We are suggesting that the direct cause for the isotope effect is a difference in electronic structure between the hydride and the deuteride, and that this electronic difference has its origin in the differences in zero-point motion of the hydrogen isotopes.

While our model is qualitative and relatively unsophisticated in its present form, it nonetheless gives a reasonable explanation for (a) the reverse isotope effect; (b) the differences (if real) in magnetic susceptibility between the hydride and the deuteride; and (c) the observed pressure effect on the superconducting T_c. Also, our model, which involves tighter binding of hydrogen than of deuterium in the Pd-H(D) lattice, is consistent with lower dissociation pressures for hydrides than for deuterides at comparable temperatures[22] and smaller negative heats of absorption[23] for the deuteride than for the hydride at comparable concentrations.

Anomalous isotope effects have been observed in other properties of the Pd-H(D) system; e.g., rates of diffusion of hydrogen and deuterium in Pd-H(D)[24] and differences in electrical resistivity[25] have not been satisfactorily explained. A full theoretical treatment of the effects of zero-point vibrational differences on the electronic structure of Pd-H(D) may shed light on these also.

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Observation of Vibrational Surface Modes in the Acousto-optical Bulk Gap of TiN

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Phonon frequency distributions of bulk $[g^b(\omega)]$ and microcrystalline $[g^m(\omega)]$ titanium nitride are obtained from neutron scattering experiments. The surface excess distribution $g^s(\omega) = g^m(\omega) - g^b(\omega)$ shows, at low energies, a positive region due to acoustic surface modes. A second positive region in $g^s(\omega)$ proves, for the first time experimentally, the existence of a band of surface vibrational modes bridging the acousto-optical gap of the bulk modes; the double-peak structure indicates two branches of surface modes.

Present knowledge on vibrational surface modes (SM) in crystals arises mainly from a still increasing number of theoretical studies.[1-6] Experimentally, optical, ultrasonic, and thermodynamic methods[1] are restricted to the long-wavelength region around the surface Brillouin zone[2] and even the most promising techniques of inelastic scattering of low-energy electrons[7] and atoms[8] up to now could be used only for studies of long-wavelength SM. The only exception is the method of inelastic neutron scattering,[9] which—applied to microcrystalline samples—yields information on surface-induced changes in the phonon density of states at all wavelengths.[5]

Especially favorable and tempting is the investigation of surface effects on a diatomic material with a gap between acoustic and optic bulk modes, as in this case the influence of free surfaces can be studied separately—to a certain degree—for acoustic and optic modes. In this paper we present the results of the first neutron scattering study in this direction. The sample material was TiN, which has NaCl structure and shows a high superconducting transition temperature; it has an electronic structure very similar to NbC and TaC, which exhibit strong anomalies in the acoustic-phonon branches.[10,11]

The TiN microcrystals were prepared by a reaction of TiCl$_4$ with NH$_3$ in an arc plasma at about 3000°C[12]; for purification, the powder was bathed in HCl and afterwards annealed at 750° in an NH$_3$ atmosphere, and then at 1100°C in a nitrogen atmosphere. Quantiative chemical analysis of the resulting microcrystalline powder determining both anions and cations exhibited excellent stoichiometry concerning the metal-to-nonmetal ratio; the nonmetal portion, however, contained 7 at.% substitutional impurities of oxygen. The size of the particles was determined by x-ray line broadening and Brunaur-Emmett-Teller adsorption; both methods gave to within very good agreement a mean particle size of 300 Å, corresponding to 4.3% surface atoms. Electron microscopy confirmed the particle size, proved narrow size distribution, and revealed mostly rectangular microcrystals with flat [probably (100)] surfaces. To prevent surface contamination the sample was first heated to 600°C at 10^{-6} Torr and then placed under argon atmosphere in a vacuum-tight container with vanadium windows suitable for neutron experiments; finally, the filled container was evacuated to 10^{-6} Torr and heated for 1 h to 130°C.

A reference bulk sample with the *same* chemical composition was prepared from the microcrystalline powder by sintering pressed pellets at 1800°C[13]; stoichiometry and composition were again determined by quantitative chemical analysis; the grain size (examined by x rays, electron microscope, and Brunaur-Emmett-Teller adsorption) was at least a factor of 100 greater than for the microcrystalline sample. This procedure assured that bulk and microcrystalline samples differed solely by the amount of surface atoms.