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Nuclear Magnetic Resonance of Hydrogen Absorbed into Palladium Wires*†

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Nuclear magnetic resonance signals have been observed for hydrogen which had been absorbed into palladium wires. Steady-state absorption and pulsed "echo" experiments were performed. The wires were connected as circuit elements and the resonance signals observed were caused by protons contained in the skin layer of the wires. Samples were loaded by means of a glow discharge to concentrations from 0.2 to 0.8 (expressed as atom ratios H/Pd). Measurements were made, as a function of temperature and hydrogen concentration, of line width, T_1, T_2, and resonance shifts. The results are interpreted to give information on the diffusion of the protons among the interstices of the palladium lattice and on the interaction of the protons with the conduction electrons. The observation of an asymmetric line shape for the absorption signal has led to a theory of a "lossy" resonance to be expected in metal wires.

I. INTRODUCTION

A. Description of the Experiment

An enormous number of investigations have been carried out on hydrogen-palladium "alloys" by means of the conventional techniques of solid state physics.[1] The present paper describes a new examination of the H-Pd system using nuclear magnetic resonance techniques. The examination consisted of nuclear magnetic resonance experiments performed on hydrogen which had been absorbed into metallic palladium wires. The loaded wires were used as integral parts of the electrical circuit and the signals observed were caused by those protons contained in the surface layers of the wires.

Pulsed and steady-state experiments were performed using the echo technique of Hahn[2] and the bridge and modulation method of Bloembergen, Purcell, and Pound.[3] The measurements made of line widths, shifts in the Larmor frequency caused by magnetic shielding, spin phase memory times (T_2), and spin lattice relaxation times (T_1) will be interpreted to give information about the relative location and state of motion of the protons and on their magnetic interactions with each other and with the conduction electrons.

B. The Hydrogen-Palladium System

It is known from conventional measurements that at least some of the occluded hydrogen atoms are mobile and that most are present as protons.[4] X-ray data[5] have indicated the coexistence of two distinct face-centered cubic phases of the palladium lattice over a range of hydrogen concentration from C near 0.1 to 0.58 (C expressed in atom ratio, H/Pd). The transition from the low concentration α-phase to the high concentration β-phase is marked by a 3.6 percent increase of the lattice parameter. Lacher[6] has been able to predict the H-Pd absorption isotherms and critical temperature from statistical considerations by assuming the existence of the occluded hydrogen as a gas of mutually interacting protons. The coefficient of diffusion has been measured for the hydrogen with widely varying results. Barrer[4] tabulates much of these data and quotes as an average value, $D=1.5\times10^{-2}\exp(-E/RT)$ cm²/sec. (Where $E=6800$ calories/gram atom.)

Palladium metal exhibits a very large paramagnetic susceptibility ($\chi_{\text{atomic}}=6\times10^{-4}$),[7] which decreases linearly as hydrogen is occluded, reaching zero at $C=0.66$[8] and remaining negligible at higher concentrations. Such behavior is explainable in terms of the band theory of metals.[9] Metallic palladium has a residual magnetization corresponding to about 0.6 Bohr magneton per atom, which implies that 0.6 electron per palladium atom are missing from the d band. One may consider each hydrogen as a potential electron donor through which the palladium seeks to remedy the d electron deficiency. Calculations have been reported[10] which indicate that a hydrogen atom dissolved in any known metallic lattice, gives up its electron because of the shielding of the proton charge by the conduction electrons. The concentration dependence described above for the susceptibility of the H-Pd indicates that, at least for $C<0.66$, each occluded hydrogen gives up its electron to the d band.

Hydrogen can be loaded into palladium from solution (by electrolysis) or directly from the ambient gas (cathodically, with a glow discharge or thermally, in an oven). Smith[1] believes that the loading is into a rift

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† Supported in part by the ONR.

[1] D. P. Smith, *Hydrogen in Metals* (University of Chicago Press, Chicago, 1948), bibliography and supplementary notes.

[2] E. L. Hahn, Phys. Rev. **80**, 580 (1951).

[3] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948) (hereinafter referred to as BPP).

[4] R. M. Barrer, *Diffusion In and Through Solids* (University Press, Cambridge, England, 1941), p. 220.

[5] See reference 1, Chapter VII.

[6] J. R. Lacher, Proc. Roy. Soc. (London) **A161**, 525 (1937).

[7] See reference 1, Chapter XIII.

[8] The value is for wires. A somewhat lower critical C has been reported for powders (reference 1).

[9] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

[10] I. Isenberg, Phys. Rev. **79**, 736 (1950).

network extending through the metal, followed by diffusion from the rifts into the lattice proper. Concentrations slightly in excess of $C=0.8$ can be attained during charging, but after the charging is stopped, the concentration drops rapidly to 0.8. A proton lattice made up of the hexagonal interstitial positions at the centers of the cube edges or one made up of alternate interstices of tetrahedral symmetry would each allow the formation of a one to one alloy with the palladium sites. Either set of interstices forms a fcc lattice with a parameter identical to that of the palladium but with different near neighbor palladium configurations for the two. A rigid lattice of the tetrahedral interstices and the palladium sites would form a structure of the sphalerite type. According to Wyckoff[11] this structure is "favored by (1) compounds with especially small cations (e.g., Be^{2+}) and (2) halides, oxides, etc., of incompleted shell transitional metals." The sphalerite arrangement might then be expected for an H-Pd alloy on both counts.

II. EXPERIMENTAL ARRANGEMENT

The dc magnetic field of about 7000 gauss was provided by an electromagnet which was constructed by Professor R. F. Paton of this department. The main current was provided by storage batteries, and an additional regulating current was controlled by a nuclear resonance detector. In the regulator the proton resonance from a frequency modulated transitron nuclear resonance detector,[12] the probe of which had been placed in the magnet gap, was fed as an error signal to a discriminator and dc amplifier. The error signal was peak-detected, permitting regulation of the central value of the field even with field modulation of amplitude much greater than the transitron signal line width. The field was measured by monitoring the central frequency of the transitron with a BC-221 frequency meter. The beat pattern between the two was fed from a communications receiver to an oscilloscope and visual observation of the zero beat allowed the field to be read and set reproducibly to ±0.02 gauss in 7000.

The radiofrequency equipment used in many of the steady-state measurements was of conventional design and was used in the general bridge arrangement of BPP.[3] The output of a crystal controlled oscillator, operating near 30 mcps, was transformer-coupled into an electrically symmetrical twin-T rf bridge. One of the two resonant arms of the bridge was a balancing dummy and the other, which was placed in the magnetic field, contained the H-Pd wire sample as a direct part of the electrical circuit. In some cases the sample had the form of a coil resonated at 30 Mc. In other instances the flexible coaxial arm of the bridge was replaced with a rigid brass coaxial line approximately a quarter wavelength long. In the latter arrangement a straight wire H-Pd sample 1.5 cm long was inserted as a terminating stub at the end of the line.

In either case the signal appearing at the bridge output was fed through a narrow band preamplifier to a communications receiver. The detected signal was then viewed on an oscilloscope or observed as the output of a narrow band phase sensitive amplifier.[3] For the measurements of line width and line shape the field was modulated at 30 cps with amplitudes near 0.02 gauss, and the center value of the field slowly varied by varying the transitron frequency.

The shifts in gauss of the center field value of the H-Pd proton resonance were measured with respect to that for water by inserting a vial of water in the coil or by simply brushing some water onto the coil or on the H-Pd stub in the quarter wave line. The apparent width of the water resonance was also used to provide a correction factor for broadenings of the H-Pd lines caused by modulation effects and magnet inhomogeneities. The apparent width of the water resonance was usually about 0.03 gauss. Both shifts and line widths could be measured to ±0.02 gauss, corresponding to the limit of accuracy of the vernier scale on the frequency meter.

Saturation studies of the spin lattice relaxation time T_1 were made by observing the deflection of the "lock-in" output meter as a function of varying rf power level.[3]

The pulsed experiments were performed with the "echo" techniques of Hahn.[2] For these measurements the rf bridge was driven by a pulsed crystal oscillator. Sequences were available of from one to four rf pulses spaced at arbitrary intervals and of durations from 7 μsec upwards. The signal from the bridge was coupled into a 30-mcps radar I.F. amplifier of MIT Radiation Laboratory design. The output of the amplifier was either detected and placed on an oscilloscope or else fed into a communications receiver which had been broadbanded to provide an attenuation of 3 db at a width of 30 kc. The additional gain and reduced band width provided by the receiver proved necessary for the observation of the very weak signals from some of the lower concentration samples.

Photographs were taken of the oscilloscope face for various pulse arrangements. T_2, the spin phase memory time, is measurable if one applies two pulses, separated by time τ, and observes, for various τ's, the amplitude of the echo signal occurring at 2τ.[2] Similarly, T_1, the spin lattice relaxation time, is measurable if one applies a third pulse at time T and observes, as a function of T, the amplitude of the "stimulated echo" occurring at time $T+\tau$. In order to improve the signal to noise ratio, each photograph represented a multiple exposure made over twenty-five repetitions of the pulse and echo sequence. The signal to noise ratio on the films was such that T_2 could usually only be measured to ±15 percent and T_1 to ±20 percent. It became quite difficult to

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[11] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948).

[12] H. W. Knoebel and E. L. Hahn, Rev. Sci. Instr. **22**, 904 (1951).

measure T_1 in those samples having the shortest of the T_2 values observed.

The data were taken between 218°K and 348°K. The magnet gap used was only $\frac{11}{16}$ in., which made the use of a Dewar vessel difficult. The low temperature control apparatus generally used consisted of a copper trough filled with CS_2 in which the samples were immersed. Copper tubing was soldered around the longitudinal edges of the trough and acetone allowed to flow at a controlled rate from an acetone-dry ice reservoir. A copper-constantan thermocouple was placed near the sample in the bath and the temperature measured with a potentiometer. The trough was insulated from the magnet pole faces by asbestos cloth.

For runs above room temperature hot water was maintained in the reservoir in place of the acetone and dry ice. The high temperature range was limited by the fact that above 70°C hydrogen is rapidly driven out of an H-Pd alloy exposed to air.

III. PREPARATION OF SAMPLES

The samples used were prepared from palladium wires of 0.030-in. diameter and >99.5 percent purity. For some of the experiments 30 cm of the wire were wound into an eight turn coil 1.2 cm long and 0.7 cm in diameter. Such coils were loaded with hydrogen by means of a glow discharge[13] to concentrations, expressed as atom ratios $C=\mathrm{H/Pd}$, from 0.2 to 0.8.

It has been observed[14] that the electrical resistance of a palladium wire increases markedly as hydrogen is absorbed. In the present work the hydrogen concentration in the H-Pd samples was monitored during the loading and subsequent experiments by measuring the resistance of the wire between two standard points. A nearly linear relation exists[14] up to $C=0.76$ between the relative resistivity, $\rho=r/r_0$, and the concentration. At $C=0.76$ the resistance has increased to the point $\rho=1.7$. As will be pointed out in Sec. IV, certain of the shifts measured in the nuclear resonance experiments essentially measured the bulk susceptibility of the alloy and provided a check on the resistance measurements of the hydrogen concentration.

The success of a loading, in terms of the C finally attained and the rate of filling, proved to be a very sensitive function of the treatment of the wire. A typical successful load began with a cleaning of the wire with acetone. The coil was then wound and placed in a vacuum system. The coil was connected as a cathode and surrounded by a cylindrical brass anode. If the wire was next annealed by electrically heating it to an orange glow in a vacuum, the loading rate was much retarded. However, if the wire was heated in about one-third atmosphere of hydrogen, the surface was "opened" [13] and an enhanced loading rate resulted. It was noted, in agreement with the findings of Ulbricht,[13] that after a wire had been heated in hydrogen, the concentration, which had increased during the heating, returned to nearly zero and no subsequent loading occurred even if the sample were allowed to remain for many days in the hydrogen. The behavior is somewhat strange in view of the success of the oven technique of loading palladium powders.[15]

The typical loading continued with a glow discharge in hydrogen at a pressure of a few cm of Hg. Such a discharge started at 300 v and 10 ma and ran for from thirty minutes to one hour, having arrived at 400 v and 4 ma at the end of that period. This electrical behavior has been described by Jacobs and Martin[16] as the result of a rise of cathode temperature. A small increase in concentration is detectable during the discharge. After the discharge hydrogen was admitted to the chamber to a pressure of some 30 cm of Hg. Full loads of $C\simeq 0.7$ were reached in times ranging from a few hours to a month. The exact role of the discharge in the loading is in some doubt. Ulbricht[13] has described the process as an activation of the surface, but it seems to the author to be more likely that the mechanism is a simple cleaning or perhaps rift-opening at the surface. It is interesting to note that successful hydrogen loads have been reported[13] following discharges in argon. Commercial grade hydrogen was generally used in the present experiments. For some loadings the hydrogen was passed through a palladium valve, but this precaution did not materially affect the loading rate or final concentration attained.

The loaded samples were removed from the hydrogen atmosphere, washed with acetone, and the experiments then performed with the wires exposed to air. This nonequilibrium situation resulted in a slow loss of charge, generally of less than 10 percent per month for a carefully handled sample. The retention of the load was perhaps aided by the formation of a surface oxide layer. The stability of the loaded wires on exposure to air in comparison to the combustibility of powder samples[15] can be attributed to the reduced ratio of surface area to volume for the wires. One might fear that the migration of hydrogen to the surface and subsequent oxidation would result in a continually replenished layer of water on the wire which might be responsible for the nuclear resonance signals observed. However, those signals will be shown in the next section to have none of the characteristics of the water resonance.

The H-Pd coils were mounted within a brass shield by crimping copper leads onto the H-Pd. No soldering was done because of the instability of the alloy under the application of heat. In the case of the quarter wavelength line technique, the sample consisted of a 1.5-cm section cut from a loaded wire and mounted in the end of the coaxial line. The line was made of $\frac{3}{8}$-in. rigid

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[13] R. Ulbricht, Z. Physik **121**, 351 (1943).

[14] See reference 1, p. 125.

[15] Torrey, Alpert, Ginsburgh, and Kohane (to be published). The existence of this independent parallel research on H–Pd alloys came to the author's attention during the course of his own work. He is much indebted to the Rutgers group for numerous discussions of data prior to its publication.

[16] H. Jacobs and J. Martin, J. Appl. Phys. **21**, 681 (1950).

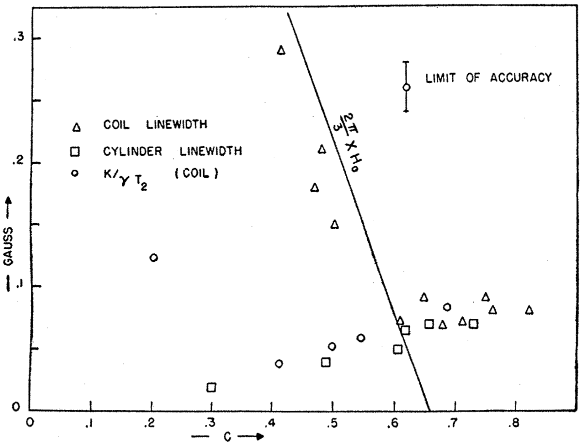

FIG. 1. Proton line width as a function of hydrogen concentration.

brass co-ax and had a 90° bend near the tip. The H-Pd alloy was placed as the center conductor in the bent tip and copper leads crimped on. The whole line could be rotated in such a manner that the H-Pd wire was oriented parallel or transverse to the magnetic field, H_0. Using as a criterion the ratio of the radius of the wire to its length, the deviation of such a sample from a true infinite cylinder can be estimated to be a few percent.

The nuclear resonance signal observed is caused by the protons contained within a surface layer of thickness the order of δ, the skin depth. δ is 1.2 mils in palladium at 30 mcps. Such a layer includes $\frac{1}{6}$ of the volume of a wire with 0.03-in. diameter. For a sample 30 cm long and a uniform proton distribution within the wire, the skin layer includes $2.8\times C\times 10^{21}$ protons. For comparison a 0.4-cc vial of water, which would just fit within the coil, contains some 3×10^{22} protons.

IV. EXPERIMENTAL RESULTS AND THEORY

A. Concentration Dependence of Line Width, T_2 and T_1

Figure 1 shows the proton line widths observed at room temperature plotted as a function of hydrogen concentration. The line widths quoted are the separation in gauss between peak deflections of the output meter of the "lock-in" amplifier, and hence, between inflection points of the resonance absorption curve. These data have been corrected for modulation and magnet broadening by comparison with the water resonance as described in Sec. II. The line widths measured above $C=0.65$ cluster about 0.08 gauss. For lower C the coil data increase with decreasing concentration and are interpreted to reflect a broadening imposed by surface demagnetization effects. A naive consideration of the variation in local field to be expected around the interior of a paramagnetic torus situated with its axis normal to H_0 leads one to expect a maximum local field excursion of $2\pi\chi H_0$, the value for the two orientations of an infinite cylinder. Further considerations, which will not be reproduced here, of the variation of the effective population of nuclear moments around the torus leads to the estimate of $\frac{2}{3}\pi\chi H_0$ for the order of magnitude of the line width observed. The solid line in Fig. 1 corresponds to $\frac{2}{3}\pi\chi H_0$ for the susceptibility data on H-Pd wires referred to in Sec. I.

The data obtained with the straight wire samples in the quarter wavelength line indicate a slowly decreasing line width below $C=0.65$ and reach the limit of accuracy of the measurements at $C=0.3$.

Figure 2 shows the concentration dependence observed for T_2 and T_1 with pulsed experiments at room temperature. A steady increase of T_2 was observed with decreasing concentration from 5.7 milliseconds at $C=0.69$ to 11 milliseconds for a sample at $C=0.41$. However, there is one much lower value of 3.6 milliseconds for the lowest concentration examined, $C=0.2$, which may correspond to an α-phase alloy.

The most striking feature of all of the above data is the narrowness of the lines or long T_2 values. One can obtain an order of magnitude for the rigid lattice line width due to a fixed array of protons which might exist in the palladium lattice. An array of the alternate tetrahedral interstitial positions forms a face-centered cubic lattice with a parameter identical to that of the palladium. Van Vleck[17] has calculated the mean square line width for a powder of randomly oriented fcc crystals to be $\langle\Delta H^2\rangle_{\text{Av}}=7.2n^2\times 2\mu^2$, where n is the number of moments per unit volume. Substitution of the value of n corresponding to the density of palladium yields a value of 3 gauss for the rigid lattice proton linewidth. The much narrower lines observed indicate the existence of rapid proton motions which cause the local fields mutually produced by the proton moments to average out to a great extent.

It is customary to write the applied rf magnetic field as the real part of $\mathbf{H}=H_1e^{i\omega t}$, and the transverse bulk magnetization as the real part of the product of $\mathbf{H}$, and the complex nuclear paramagnetic susceptibility $\chi_{\text{nuc}}=\chi'-i\chi''$; thus, $M=H_1(\chi'\cos\omega t+\chi''\sin\omega t)$. The power absorption in a nuclear resonance experiment may be written

$$P=v\int_{t=0}^{v}\mathbf{H}\cdot d\mathbf{M},$$

and since we are interested only in changes in the amplitude of $\mathbf{M}$, the integral gives $P=\frac{1}{2}\omega H_1^2\chi''$ ergs/mole second. The functional dependence of χ'' on ω thus gives the shape of the absorption mode of the resonance. Pake and Purcell[18] define a shape function by

$$\chi''(\nu)=\pi\chi_0 g(\nu),$$

$$\int_0^\infty g(\nu)d\nu=1,\quad\text{and}\quad T_2=\tfrac{1}{2}g(\nu)_{\max}.\qquad(1)$$

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[17] J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

[18] G. E. Pake and E. M. Purcell, Phys. Rev. 74, 1184 (1948).

For a given line shape there exists a unique relation between T_2 and the line width measured between inflection points of the $\chi''(H)$ curve, $\Delta H = K/(\gamma T_2)$, where γ is the gyromagnetic ratio and K has the value $2/(3)^{\frac{1}{2}}$ for a Lorentzian line shape or $(2\pi)^{\frac{1}{2}}$ for a Gaussian.[19]

If one simultaneously considers the line width and T_2 data reported here, a discrepancy is evident. The $K/(\gamma T_2)$ points plotted in Fig. 1 were calculated from the T_2 data of Fig. 2 using the arbitrary value $K=12$. The significance of the result is not clear. It is difficult to accept the large number and the peculiar sharp-shouldered line that it implies, especially since no such line shape was observed. The discrepancy has led the author to examine the data for a few other solids that are suitable for both pulsing and steady-state measurements. Values of K of the order of 10 were obtained from crude preliminary data taken on paraffin, rubber and metallic sodium, and lithium. It must be pointed out that (contrary to the case in liquids[2]) in all of these measurements on solids, the noise present was such as to prevent a definite determination of the exponential character of the echo decay envelope. The time constants were measured by drawing a best straight line through the data plotted on semilogarithmic paper. Bloch's equations,[20] which assume a Lorentzian line shape, have been used in the analysis[2] that gives T_2 as the time constant for the spin echo decay. The more general case of non-Lorentzian lines has not been treated in the literature.

B. Skin Effects

An asymmetric line shape was observed during the line width measurements. If the rf bridge was so balanced with a vial of water in the coil as to present a pure absorptive mode ($d\chi''/dH$) on the output meter and then the water removed and the bridge balanced to the same criterion of detected voltage, then the H-Pd resonance line was observed to be somewhat dispersive in shape. If the bridge was balanced for an absorptive H-Pd signal at a low rf level, then the signal rapidly acquired a dispersive component upon increase of the rf voltage. The bridge was always rebalanced to present a symmetric line shape before a line width measurement was made.

In order to show that the asymmetric shapes observed were not the result of slight shifts of the bridge balance, the experiment was repeated using a transitron detector[12] to drive the coil instead of the bridge and fixed oscillator. Although the transitron device detects only those voltages in phase with the resistive (normally χ'') component, the same asymmetric line was observed for the H-Pd signal. The effect was shown not to be caused by the bulk paramagnetic susceptibility of the palladium, since similar shapes were observed for concentrations above and below 0.66. The effect was also observed for the straight wire samples as well as for the coils.

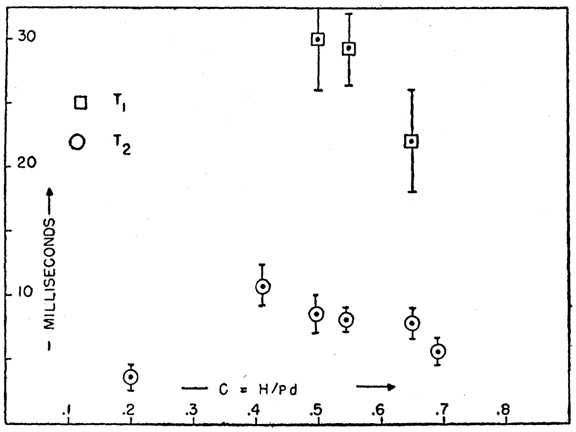

FIG. 2. Room temperature values of T_1 and T_2 as functions of hydrogen concentration.

The reason for the dispersive component of the resistive nuclear signal becomes clear if one considers that the resonance signal was caused by protons contained within a metallic conductor having finite conductivity. There was therefore no unique phase for the rf current within the wire, a phase shift of $\pi/2$ in fact being attained at a depth equal to the skin depth, δ. Physically, the penetration is limited by χ', the real part of the nuclear susceptibility, and the resulting ohmic losses produce a skewed resonance.

Slichter has carried out calculations, which will not be reproduced here, showing the existence of a dispersive component to the resistive signal from a wire, the change in the coil resistance turning out to be proportional to $\chi'+\chi''$. A simple calculation of the saturation behavior was made based upon a step function model for the nuclear susceptibility within the wire with a saturated region, where χ_{nuc} is taken to be zero, existing near the surface. The relative amount of the dispersive component was shown to be a function of the rf voltage. Using a saturation criterion indicated by the theory, a comparison of saturation runs made on H-Pd and on water led at first to erroneous estimates of T_1 of the order of 1 second.[21]

A more nearly exact calculation has since been made based upon the representation of χ_{nuc} by a linear rise from zero in the saturated region near the surface over a distance 2δ to the unsaturated value. At the halfway point of the rise the rf field H_1 has attained the critical value for the onset of saturation; $H_1(\text{crit.}) = (1/\gamma^2 T_1 T_2)^{\frac{1}{2}}$ and χ'' has decreased by one-half. The application of this model results in saturation values for T_1 which are in agreement with the results of the pulsed experiments.

Pake and Schuster of Washington University have kindly provided the author with additional verification

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[19] N. Bloembergen, *Nuclear Magnetic Relaxation* (M. Nijhoff, The Hague, 1948).

[20] F. Bloch, Phys. Rev. **70**, 460 (1946).

[21] R. E. Norberg, Phys. Rev. **81**, 305 (1950).

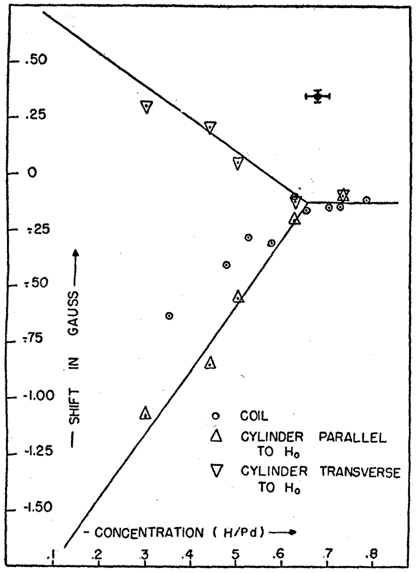

FIG. 3. Shift of H–Pd proton resonance, with respect to that in water, as a function of orientation and of hydrogen concentration.

of the theory. They have a nuclear resonance spectrometer detecting only the resistive mode with which they have obtained a tracing for the quadrupole-split Al^{27} resonance in a crystal. The tracing shows an incidental Cu^{63} resonance, caused by the copper coil, with excellent signal to noise ratio and of clearly asymmetric shape. Similar effects should be observed in metal powders for which the ratio of grain size to skin depth is sufficiently large.

C. Resonance Shifts

Figure 3 shows relative shifts of the H-Pd resonance as a function of C. The shifts were measured with respect to the proton resonance observed in water which had been brushed onto the sample or (for the coil) placed within it. The shifts measured with the quarter wave method were obtained with the sample in two orientations, i.e., with the cylinder axis normal to and parallel to the applied dc magnetic field. The shifts measured for concentrations below 0.65 thus correspond to resonance measurements made within a nearly infinite paramagnetic cylinder which had been oriented in an external magnetic field. The straight lines drawn correspond to $H_0[1+(4\pi\chi/3)]-H'$ and $H_0[1+(4\pi\chi/3)-2\pi\chi]-H'$, respectively, where H' is the small shift observed at high concentrations and the susceptibility data are those referred to in I. The $-2\pi\chi H$ demagnetization term has been added to the Clausius-Mossotti local field relation to take into account the effect of the surface magnetization induced in the transverse orientation. The fact that the data fall so closely along the lines indicates that in H-Pd the local field contribution from the very near-neighbor dipoles included in the Lorentz sphere is negligible.[22] The agreement was sufficiently good to provide a rough check on the resistanec-measured values of hydrogen concentration.

The shifts observed with the coils for C below 0.65 also are of the right sign and order of magnitude to be attributed to surface demagnetization effects rather than to any nuclear interactions. All of the shifts observed below $C=0.65$ exhibited a $1/T$ temperature dependence within experimental error. Since χ for the palladium goes nearly as $1/T$ in the temperature interval in question, the behavior provides further evidence of the bulk character of the effects.

The shift, ΔS, measured for $C>0.65$ appears independent of concentration and agrees for both coil and straight wire samples. This high C shift averages 0.12 ± 0.03 gauss and represents a percentage shift of $\Delta S/H_0=0.0017$ percent. The shift is paramagnetic and appeared independent of temperature within experimental error. The shift is interpreted to be of the type observed by Knight[23] arising from interaction of metallic nuclei with the conduction electrons. The small size of the shift in H-Pd indicates the existence of a small amplitude of the electron wave function at the protons.

D. Temperature Dependence of Line Width, T_2 and T_1

Figures 4 and 5 show the temperature dependence observed for line width, T_2 and T_1 between 218°K and 303°K. Again in Fig. 4 as in Fig. 1, the $K/(\gamma T_2)$ curve gives a reasonable fit to the line width data only with an abnormal value for K. The points plotted are for $K=12$. All of the samples were observed to exhibit a line width which broadened with decreasing temperature. One sample (not shown) with a concentration near 0.8 reached a line width of 0.6 gauss at 230°K. Pulsed data were not taken on any samples with $C>0.69$. Figure 5 is a composite of T_1 and T_2, values

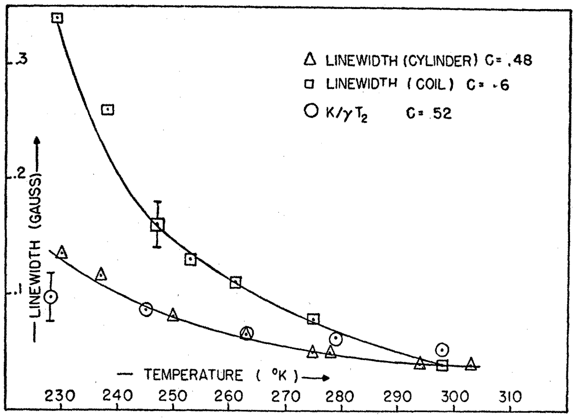

FIG. 4. Temperature dependence of proton line width for several hydrogen concentrations.

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[22] W. C. Dickinson, Phys. Rev. 81, 717 (1951).

[23] W. D. Knight, Phys. Rev. 76, 1259 (1949); Townes, Herring, and Knight, Phys. Rev. 77, 852 (1950).

taken for each of two samples with C near 0.52. The data indicate the existence of a T_1 minimum near 250°K.

It has proved possible in other metals, which exhibit a sufficiently narrow line to allow the application of the pulsing technique to interpret[24] the T_2 data in terms of an extension of the theory of relaxation times in liquids developed by BPP.[3] Such an analysis has yielded a reasonable value for the coefficient of self-diffusion for sodium nuclei. The theory predicts the existence of a T_1 minimum in the absence of other relaxation mechanisms when the characteristic frequency associated with the random fluctuations of the relative coordinates of the diffusing nuclei is nearly equal to the Larmor frequency for the nuclei. One may define a correlation time τ_c for a pair of nuclei as the time necessary for the local field of one nucleus at the other to change appreciably. For two diffusing nuclei this time is that required for diffusion over a distance of the order of the initial separation. Such a definition results in an exponential temperature dependence for the correlation time

$$\tau_c=1/\omega_c=r^2/12D, \tag{2}$$

where, conventionally, $D=D_0\exp(-E/RT)$.

Bloembergen[19] analyzes the spin-lattice interaction in terms of a Fourier analysis of the spectrum of translational fluctuations of the coordinates and obtains the expression,

$$\frac{1}{T_1}=1.6\pi n\gamma^4\hbar^2 I(I+1)\times\int_{r_1}^{\infty}\frac{1}{r^4}\left(\frac{\tau_c}{1+\omega_0^2\tau_c^2}+\frac{2\tau_c}{1+4\omega_0^2\tau_c^2}\right)dr, \tag{3}$$

where n is the number of nuclei per unit volume and r_1 the distance of closest approach. For $\omega_0^2\tau_c^2\ll 1$, which apparently corresponds to our room temperature case, the expression becomes

$$1/T_1=0.4\pi n\gamma^4\hbar^2 I(I+1)/Dr_1. \tag{4}$$

For $n=C\times$atom density of Pd, (4) reduces to

$$1/T_1=3.16\times10^{-14}C/Dr_1. \tag{5}$$

Substitution in (5) of the room temperature value $T_1=0.03$ sec for $C=0.53$ and taking as the lower limit of integration the separation of the tetrahedral wells of the Pd lattice, $r_1=2.8\times10^{-8}$ cm, yields the result $D=1.8\times10^{-8}$ cm²/sec. The value is an order of magnitude less than that computed from Barrer's[4] averages, $D=1.8\times10^{-7}$ cm²/sec.

If one plots the T_1 data of Fig. 5 on a logarithmic scale *versus* the reciprocal of the temperature and draws a best straight line through the data above 250°, the slope of the line corresponds to an activation energy $E=3.7\pm1$ kcal/gram atom. The value is considerably less than the average quoted by Barrer, $E=6.8$ kcal/gram atom. The values $D=1.8\times10^{-8}$ and $E=3.7\pm1$ yield an order of magnitude for D_0 of $10^{-5\pm1}$ cm²/sec. Such a small D_0 has been interpreted by Zener[25] to indicate that the main mechanism of diffusion is via "short circuit" paths along lattice imperfections.

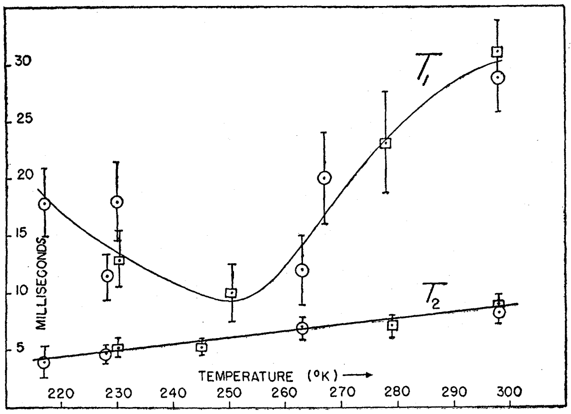

FIG. 5. Temperature dependence of T_1 and T_2. Composite curves for two samples with C near 0.52.

Professor Torrey[15] has performed an analysis of the H-Pd relaxation processes, among which he includes the effect of rift diffusion. It is possible to fit the Rutgers data by the results of his theory. The Rutgers data were taken at 9 mcps with H-Pd powders and indicate a minimum of 13 milliseconds near 240°K for a sample with $C=0.64$. Their lower Larmor frequency leads one to expect that the temperature of the T_1 minimum should be shifted downward about 20° from the 250° reported here.

The mechanism that usually determines T_1 for metallic nuclei is interaction with the conduction electrons. Korringa[26] has derived a relation between the Heitler and Teller[27] expression for T_1 in a metal and the Townes, Herring, and Knight[23] expression for the metallic shift,

$$1/T_1=(\Delta S/H_0)^2(\pi kT/\hbar)(\gamma_{\text{nuc}}/\gamma_e)^2. \tag{6}$$

Substitution of the shift, $\Delta S/H_0=1.7\times10^{-5}$, observed at high concentrations yields a value for the electron-induced T_1 of the order of two seconds. The very large T_1 and the predicted $1/T$ temperature dependence apparently exclude interaction with the conduction electrons as the source of the proton T_1 observed for C near 0.5.

E. Discussion of the Line Widths

Since T_1 is greater than T_2 at room temperature, it appears that there exists a broadening of the line width beyond that determined by spin-lattice interactions. The broadening may be described in terms of a time T_2' so defined that $1/T_2'=1/T_2-1/T_1$. Application of

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[24] R. E. Norberg and C. P. Slichter, Phys. Rev. **83**, 1074 (1951).

[25] C. Zener, J. Appl. Phys. **22**, 372 (1951).

[26] J. Korringa, Physica **16**, 601 (1950).

[27] W. Heitler and E. Teller, Proc. Roy. Soc. (London) **A155**, 629 (1936).

this expression to the data of Fig. 5 results in a value of T_2' near 0.012 second over most of the temperature range investigated. The exact source of this broadening is not clear.

The mechanisms which are the most likely competitors for the determination of the observed line widths include: mutual interactions among the proton moments or of the proton moments with the conduction electrons and the palladium nuclei or the *d* electron vacancies. For $\omega_c > \omega_0$, (which the T_1 data indicate to be our room temperature case) the simple liquid theory of mutually interacting proton moments predicts that T_2 be of the order of T_1.[3] Furthermore, a broadening independent of temperature would not be expected until the rigid lattice line width had been reached. The application of the liquid model to H-Pd may be naive in the use of the separation of lattice interstices as the lower limit of the radial integration or distance of closest mutual approach of the occluded protons. Even if the diffusion is primarily a lattice diffusion, the theory assumes spherical symmetry and neglects the existence of lattice-imposed restrictions on the relative coordinates of near neighbor protons. Also, it may be that T_2 is determined by a combination of spin-spin relaxation associated with a local order-disorder jumping of the protons among nearby wells and an additional static line broadening caused by long range interaction with the more distant proton moments.

The T_2 measurement made at $C=0.2$ may correspond to the α-phase of the alloy. The α-phase diffusion coefficient would be expected to be less than that for the β-phase since the lattice has not yet undergone the 10 percent volume expansion. The fact that the β-phase T_2 is less than that observed for higher concentrations may indicate that the broadening, T_2', is sensitive to the state of diffusion or it may simply reflect a reduction in T_1. The signal to noise ratio attainable with the low concentration sample was so small as to prevent a reliable measurement of T_1.

Among the other possible interactions we may discard any effects caused by nuclear magnetization of the palladium on the following grounds. All the Pd isotopes except Pd^{105}, which occurs in 23 percent abundance and whose moment is not known, are even-even nuclei and cannot on present theory have nonzero moments. In addition to the abundance factor of $\frac{1}{4}$ there is a factor of 5/9 to be considered in the effectiveness of nonidentical nuclei in the interaction theory.[17]

The line broadening arising from the interaction of the protons with the *s* conduction electrons amounts to a negligible fraction of the line widths observed since the electron-induced $T_1 \simeq T_2$ has been calculated in Sec. IV-D to be of the order of a second. The interaction with the *d* electron vacancies is similar to that with ordinary conduction electrons rather than to an interaction with paramagnetic ions. Since the mobility of the vacancies is large compared to that of the protons, the interaction may be described as occuring with a small effective electron moment. The interaction may be diminished by the filling of the vacancy nearest to any given proton by the electron originally associated with that proton. T_2' arising from the interaction with the *d* vacancies should increase with increasing hydrogen concentration.

SUMMARY

The experimental data for T_1, T_2, and line widths indicate that the occluded protons are moving rapidly within the metal. The application of a relaxation theory based on a simple model which represents the motion as self-diffusion in a proton liquid results in good qualitative, but only fair quantitative, agreement with the data. The theory, which has previously been shown to yield good results for self-diffusion in metallic sodium would be defective in the H-Pd case if the proton diffusion occurs primarily via lattice imperfections. The small value of D_0 estimated from the data would support such a "short circuit" diffusion hypothesis.

Relaxation mechanisms based on phenomena other than the mutual interactions of the proton moments may be excluded on the basis of the above data and the measurements of resonance shifts.

The wire sample technique has certain convenient features for the experiments, notably in the "infinite cylinder" measurements. In these same measurements, however, the primary defect of the technique, a small signal to noise ratio, is at its worst. Work is currently in progress in our laboratory on narrow band equipment for observing the echo phenomena which, it is hoped, will result in a significant increase in the attainable signal to noise ratios. With such equipment the wire sample method might be applicable to nuclear resonance investigations of systems related to H-Pd, such as D^2-Pd, Cu-Ni, and Ag-Pd.

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