

The Palladium-Hydrogen System

PART II OF A SURVEY OF FEATURES

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This article completes the review of the relationship between equilibrium pressure and composition, which was started in the first part of the paper, before going on to consider some other aspects of the hydrogen-palladium system.

Studies by a number of investigators (23,35, 90) have been concerned with hysteresis differences between absorption and desorption p-n relationships, and the extent of hysteresis on the macroscopic form of the specimens. Similarly to findings of Frieske and Wicke (27), measurements of Evans and Everett (90) and Everett and Sermon (23) have shown that the extent of hysteresis loops is reduced with decreases in the overall sizes of specimens. Recent studies with evaporated films (92) have indicated that with decreasing thickness of the films there is a complementary decrease in the range of values of n over which there is virtual invariance of equilibrium pressure indicative of the major part of the $\alpha \rightarrow \beta$ phase transition. Further careful studies of p-n relationships obtained in the course of absorption and desorption cycles limited to ranges of hydrogen content within the main hysteresis loop have recently been reported (24,99).

In α phase regions, the use of ultra-high vacuum techniques (20,21) has made it possible to obtain accurate determinations of p-n relationships at very low hydrogen contents with bulk specimens without special activation procedures. This has led to accurate appreciations of errors in p-n relationships resulting from significant amounts of adsorption on

dendritic surface layers (20,100), or from incorporation of hydrogen at internal surfaces of voids or, seemingly more importantly, at dislocations (94,99).

Discussions concerning the onset of $\alpha = \beta$ phase transitions have stemmed from a study of correlations between hysteresis of electrical resistivity against hydrogen content relationships, and complementary hysteresis of p-n relationships derived for a series of temperatures over the range 0 to 85°C, from measurements of electrode potential (47). The convenient interconvertibility of equilibrium hydrogen pressures and electrode potentials measured at suitably activated electrodes, from considerations of their common equatibility to hydrogen chemical potential, also has been further illustrated by studies of electrode potentials in conjunction with electrical resistivities at temperatures and pressures of up to 200°C and 27 atmospheres, respectively (101). These measurements have formed a background for the continued development of hydrided palladium electrodes as a means of determining hydrogen ion concentrations (102).

In addition to further studies of p-n relationships with deuterium, which have accompanied some of the more recent p-n measurements with hydrogen (20,90), quite extensive studies and discussions (93,103-105) also have appeared concerning separation factors referring to distributions of mixtures of hydrogen and deuterium between the gaseous phase and hydrides in either the α , $\alpha + \beta$ or β phase composition ranges. Separation factors determined from equilibria involving hydrogen and tritium have been employed to derive p-n relationships in the β phase region of the palladium-tritium system (106). The various

data have quite recently been reviewed in conjunction with information available for equilibria in which there is the further involvement of H_2O and D_2O (53,104)—where measurements so far available do not seem to be completely consistent and have a bearing on the interpretation of electrolytic hydrogen isotope separation factors (53).

Thermodynamic Functions and Calorimetric Measurements

The additional studies of p - n relationships, at various temperatures, have enabled parallel extensions of information to be made concerning partial molar entropies and heats of absorption and desorption of hydrogen. There has been particular interest in estimations of these partial molar quantities at the initially lowest contents of hydrogen, n (infinite dilution) and in subsequent deviations from Sievert's Law ($n \propto p^{1/2}$) from the standpoint of estimating values of energies of attractive interaction between hydrogen interstitials which have been correlated with the $\alpha = \beta$ phase transitions. These factors have had an important bearing with regard to models proposed to account for the forms of the p - n relationships of the palladium-hydrogen and palladium alloy-hydrogen systems. Substantial reviews of these aspects have quite recently appeared (1,104,107,108). There also have been a significant number of calorimetric studies. At very low temperatures, specific heat measurements have been made with objectives of improved understanding of electronic structures both for very low hydrogen contents (109) and also at very high contents which have revealed effects arising from the superconducting state (48,61).

Recent calorimetric measurements of heats of hydrogen absorption have been complementarily made in conjunction with p - n determinations, including some at rather high temperatures (22,110) and others at quite low temperatures with surfaces of acceptably high activity for hydrogen absorption, achieved under ultra-high vacuum research conditions.

The diagrammatic plot in Figure 3(c) represents what has seemed to be (112) a prob-

able general trend of change of partial molar heats of formation with hydrogen content at 25°C. The existence of the initial minimum in this plot has been suggested by the findings of decreases in heats of adsorption with hydrogen coverage and increases of heats of absorption over the α -phase region (20,21,112,113). The form of the relationship in Figure 3(c) over the approximate region of the onset of the $\alpha \rightarrow \beta$ transition would latterly (47) seem as likely to correspond with some initial measure of β phase formation as to gradual changes of structure (112). In purely β phase regions the decrease of heats of absorption with increasing n seems reasonably well confirmed (112,113), although some studies (90) suggested a temporary increase at the upper limit of the $\alpha \rightarrow \beta$ phase transition.

High Hydrogen Contents in β Phase Hydrides

Quite recent direct estimates of changes of hydrogen content, at 25°C, under very high hydrogen pressures (25,45) have shown an incorporation of hydrogen into β phase structures up to values of n which closely approach unity. Earlier however, a continuation of absorption of hydrogen into the β phase at up to equally high hydrogen pressures had been indicated from measurements of thermoelectric power (114), Hall Effect (115) and, initially (45,69,116), by the decreases of electrical resistivity illustrated in Figure 4. The subsequent findings of superconducting transitions at low temperatures for high values of n (45,46,48,49,61,69,117) were mainly responsible for the increased interest in attaining high hydrogen contents by the various techniques compared above (34,40,45,46,49,61).

There has been recent interest in preparing samples of β phase composition for which an $\alpha \rightarrow \beta$ transition has been avoided by loading with hydrogen at temperatures above the generally accepted critical temperature with respect to α and β phase coexistence and then cooling under a sustained high pressure of hydrogen (29,32,33,36,48). Care is however needed to restrict subsequent hydrogen loss and

complementary introduction of defects (34,40) during any later measure of $\beta \rightarrow \alpha$ transition.

α Phase Structures in the System

Over the low range of values of hydrogen contents corresponding to α phase compositions, X-ray crystallographic studies have so far only been interpreted as indicative of a small increase of the overall value of the f.c.c. lattice parameter (4,23,47).

Results of diffuse neutron scattering experiments (29,118) and of fast ion channelling (28) have however centred more attention on the position and behaviour of individual hydrogen interstitials. These studies (28,118) have shown, as in β phase structures (4-11,23,47), that the hydrogens (deuteriums) occupy octahedral interstitial sites. Vibration amplitudes of the hydrogen in these octahedral sites have been determined (28,118), although it has not yet seemed possible exactly to assess proposals (119-121) that local retractions of adjacent palladium atoms should be of similar magnitude to those in β phase structures.

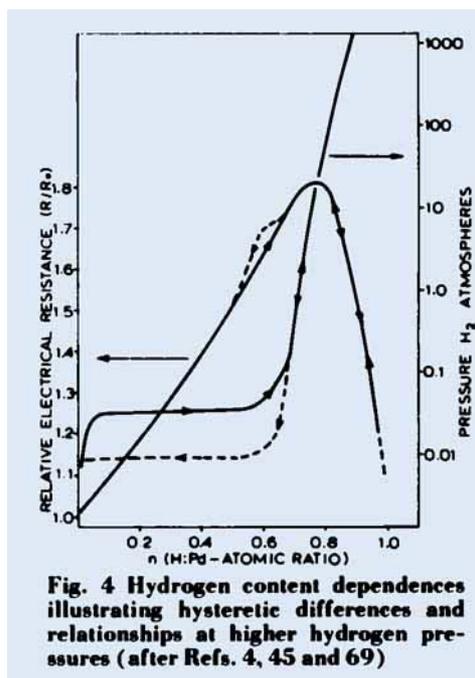
The $\alpha = \beta$ Phase Transitions and Associated Hysteretic Effects

The major portion of regions of $\alpha = \beta$ phase transition have been characterised by virtual constancy of equilibrium hydrogen pressure or electrode potential (4,23,27,47,90,104,113), and an important associated feature of the transitions is the existence of a hysteretic difference of hydrogen chemical potential between the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ regions as illustrated by examples in Figures 3 and 4. Also shown are examples of parallel hystereses of relationships between hydrogen content and physical properties such as magnetic susceptibility (27,104) in Figure 3(b), and electrical resistivity (4,47) in Figure 4. Other experimental techniques and parameters providing evidence of coexistence of the two phases and delineation of hysteresis loops include X-ray crystallography (4,23,47) and recent studies of Knight Shifts (35), electron spin resonance (31) and neutron radiography (54). Compositions of the respective phases in

coexistence, most recently have been estimated (27,104) by extrapolations of relationships established between hydrogen contents and experimental parameters, over regions where coincidences of absorption and desorption relationships have suggested that only purely α or β phase should be present.

Nevertheless exact points of onset of the transition have been difficult to estimate and recently attention has been redrawn (47) to less chemical potential independent regions at both ends of hysteresis loops where X-ray studies (122) provide evidence that α and β phase regions begin to exist in conjunction even before the main regions of transition—and would not seem inconsistent with recent calorimetric measurements (24) during cycles of partial desorption and reabsorption within the main part of the loop. Thus Figure 5 illustrates how faint reflections characteristic of the forming phase at 100°C, would seem to have been observed before main regions of transition corresponding to changes of electrical resistivity.

These recently drawn correlations (47) have some particular interest in view of continued



speculations (4,22-24,27,74,90,98,99,104,107, 111,113,123) concerning the origins of hysteresis and also concerning which, if either (4,27,104,113), branch of the hysteresis loops in p-n relationships may represent equilibrium conditions. The recent reassessments (47) appear to suggest that effective equilibria are likely to have been established at all parts of hysteresis loops, at hydrogen chemical potentials governed by internal conditions of stress—as dictated by the direction of the phase transformation and by the shape and dimensions of the specimen.

Relationships at Critical and Supercritical Temperatures

A formal characterisation of the critical p-n isotherm with respect to α and β coexistence has been the presence of a point of inflection corresponding to zero values of the first and second differentials of hydrogen chemical potential with respect to content, and values of critical parameters continue to be important in attempts to fit forms of experimental p-n isotherms to theoretical models of the system (4,26,36,95,104,107,108,112,120,121,124,125). Some need for closer consideration of what had been thought to be critical or supercritical regions with respect to phase transition in metal-hydrogen systems has, however, been indicated by several recent crystallographic and anelastic studies (98,124,126,127).

Critical, $T_{c(\alpha, \beta)}$, and higher temperature, supercritical, isotherms have been associated (4,26,27,36,47,68,74,81,98,104) with eliminations of hystereses and homogeneous distributions of hydrogen at all contents. But, as may be gauged from Figure 3(a) the forms of p-n isotherms for the palladium-hydrogen and palladium alloy-hydrogen systems (26,27,36,68,69,74,104,128,129) have been found to continue to exhibit wide ranges of hydrogen content with only very small changes of hydrogen chemical potential, at temperatures substantially higher than values of $T_{c(\alpha, \beta)}$, as suggested by the virtual absence of hysteretic effects. This, combined with further consideration of complementary relationships between

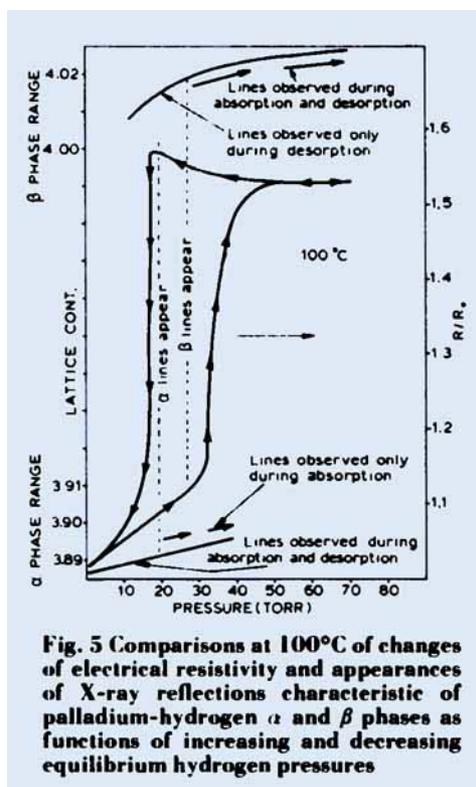


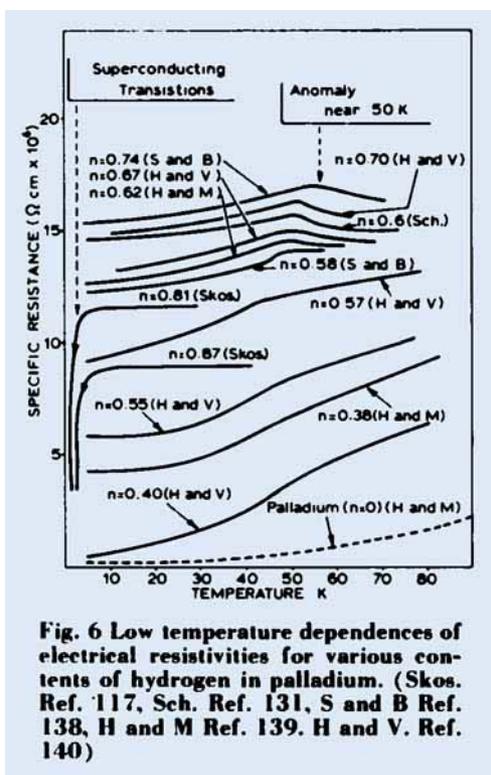
Fig. 5 Comparisons at 100°C of changes of electrical resistivity and appearances of X-ray reflections characteristic of palladium-hydrogen α and β phases as functions of increasing and decreasing equilibrium hydrogen pressures

Effects at Low Temperatures

electrical resistivity and hydrogen content (96-98,127,128), has seemed to suggest the possibilities of a retention of some measures of lattice order at higher temperatures than have heretofore been carefully considered.

A number of further studies have been made in recent years, either wholly or partly related to the anomaly near 50K in plots of specific heat against temperature; and several other experimental parameters have now been examined over adjacent temperatures (4,30,32,34,40,45,46,48,49,61,104,130-132).

One explanation of the anomaly has been that it is associated with a structural transition (other low temperature transitions in the palladium-iron-hydrogen system also have recently been suggested (133)) and modifications of phase relationships have been proposed (134), although not with any associated forms of p-n relationships. Although no structural



evidence of a transition near 50K has so far been obtained from X-ray studies (135), structural changes have quite recently been observed by using neutron diffraction techniques (136,137).

Electrical resistivity has latterly been an extensively studied parameter (47), especially at very low temperatures.

A peak observed (4,45,48,131,138-140) at intermediate hydrogen contents and in a similar temperature range to the specific heat anomaly is shown in Figure 6. In general similarity (40,49) to the relationship in Figure 4, Figure 6 illustrates substantial decreases of resistivity for $n \geq 0.74$, and superconducting transitions were observed (117) which have aroused much interest (30,32,34,40,45,46,48,49,61,104,141-143). Changes of the temperature of the superconducting transition have been studied as functions of hydrogen and deuterium contents (46,141), and it seems that deuterium produces slightly higher transition temperatures than

hydrogen (protium) for the same atomic contents. With increasing content of either isotope there is a gradual increase of transition temperature up to 10 or 12K at values of $n = \text{H(D):Pd}$ very near unity, although a final small decrease of transition temperature seems probable at the very highest values of n .

Electronic Properties and Chemical Binding Considerations

From earliest findings of continuance of metallic characteristics at high hydrogen contents (4,5) it has been hypothesised that hydrogen in palladium behaves either as a metallic allotrope (144), or as an alloying element behaving as a proton, and contributing electrons to the overall electronic structure (27,43,104,108,125,145). The latter line of interpretation has seemed to be supported by apparent similarities in the effects of hydrogen, to the effects of alloying silver with palladium—including, in particular, decreases in paramagnetism. A protonic nature of hydrogen has also seemed to be indicated by migration of hydrogen to the cathode under an electric field (145) and recently has seemed to allow interpretations of diverse experimental parameters such as De Haas-Van Alphen oscillations (146) and electron/positron annihilation effects (147). Assumptions of a protonic nature of the hydrogen have, however, tended to understate problems of allowing for either localised or overall lattice expansions—equivalent changes of which, when produced thermally, could be expected (148) to produce effects on paramagnetism similar to those of electron transfer. Difficulties in making accurate allowances for lattice expansions in theoretical calculations of electron band structures have been increasingly appreciated (149,150). Also, more widely realised have been the limitations of comparisons drawn from dependences on silver content of the solubility of hydrogen in palladium-silver alloys, in view of their marked variations with changes of temperature and pressure reference (37,96). Again, with regard to studies under an applied electric field, migration of hydrogen towards

the cathode has been found to occur in hydrides of Group IV and V transition metals (151) which otherwise have provided evidence for the view that the hydrogen in metallic hydrides is a more marginally anionic than protonic entity (8,119,148,152). Further arguments in support of this alternative view have been derived (119) from recent evidence (75,153-155) of the high pressure formation by rhodium of a hydride analogous to β phase palladium-hydrogen, in view of other evidence that hydrogen is generally at the negative end of rhodium-hydrogen dipoles (119) and also, indeed, in surface palladium-hydrogen dipoles (156). Within such a general model differences in results of interactions of hydrogen with palladium and, for example, its companion elements platinum and nickel might be thermodynamically accountable in terms of differences of atomic sizes and elastic constants (50).

Dimensional Changes on Hydrogen Absorption and Desorption

As already emphasised, the continuing central feature of the palladium-hydrogen system is the retention of metallic characteristics essentially quite similar to those of palladium alone, despite the substantial volume expansions resulting from hydrogen incorporation. These volume changes are reflected by increases in the f.c.c. lattice constants (4,23,45,47,104,122,129,135,157) but also can be directly appreciated by macroscopic changes of dimensions (4,34,36,47,54,98,158,159).

The results of recent measurements by F. M. Mazzolai, made in conjunction with studies of elastic and anelastic properties (34), of changes of overall volumes (the hydrostatic balance, water displacement technique) and external dimensions of rectangular cross-sectioned palladium bars over the course of a cycle of increasing and decreasing hydrogen content are illustrated in Figure 7. The volume/content relationship is in good agreement with one calculated from X-ray data although, in slight contrast to an earlier general plot (157), the region of approximate linearity continues over the entire β phase region studied.

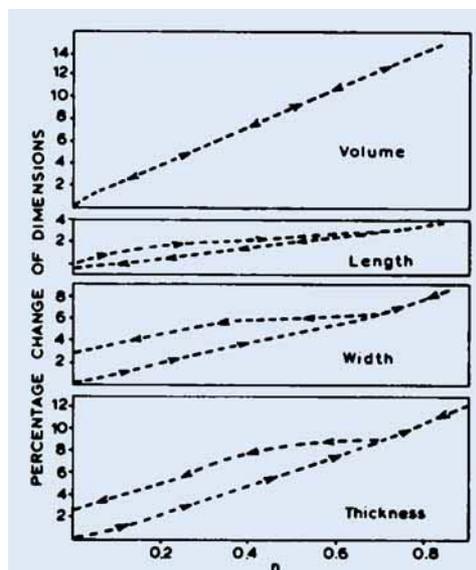


Fig. 7 Dimensional changes of palladium bars during absorption and desorption of hydrogen (after Ref. 34)

The relationships in Figure 7 have suggested slightly larger incremental volume expansions in the initial low hydrogen content, α phase, regions. This might be interpreted as indicating a slightly greater distension than in the β phase of vacant interstices adjacent to those occupied; and thus perhaps provide an impetus for complementary reductions of stress by formation of β phase regions. Even small differences between volume/content relationships of the two phases should be expected to be reflected by hysteretic differences between absorption and desorption, because of differing proportions and contents of α and β regions over $\alpha = \beta$ transitions (47). No such effect has been detected, however.

The clearly detectable irreversible changes of external dimensions produced by an $\alpha = \beta$ cycle is shown in Figure 7. In general keeping with previous observations (4,158) the average length of the specimen has contracted while both average breadths and thicknesses have been increased. The average macroscopic dimensional changes represent a gradual distortion of specimen shape (4,158) accompanied

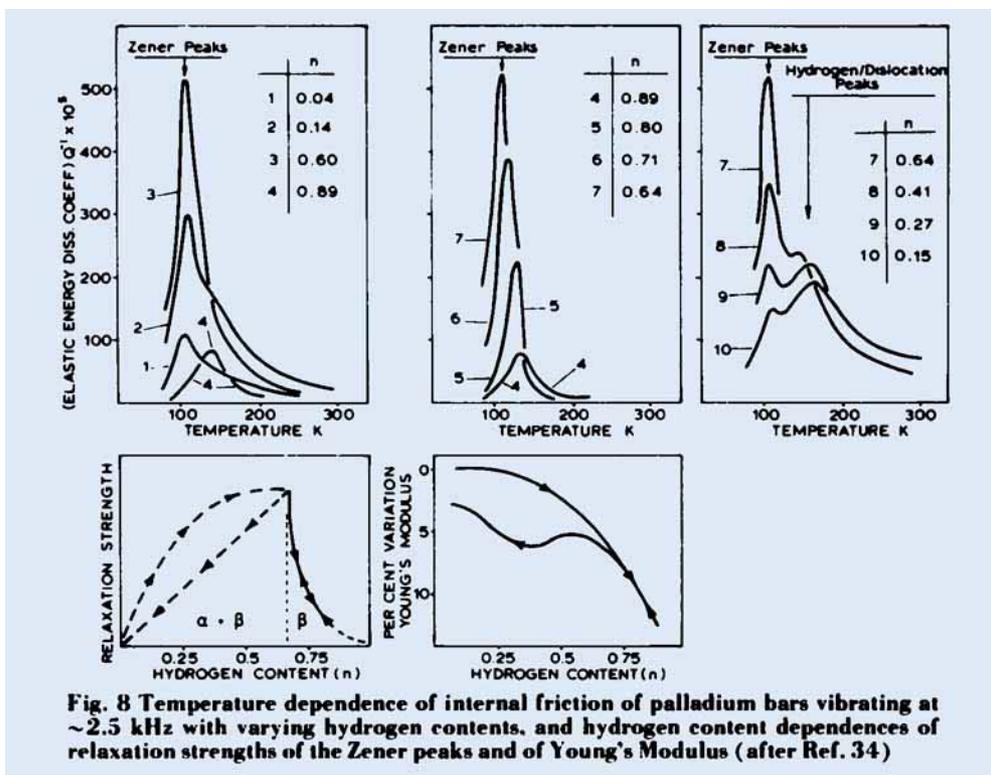


Fig. 8 Temperature dependence of internal friction of palladium bars vibrating at ~ 2.5 kHz with varying hydrogen contents, and hydrogen content dependences of relaxation strengths of the Zener peaks and of Young's Modulus (after Ref. 34)

by developments of surface irregularities (4), latterly shown to include development of extensive tangles of dislocations (160,161). These surface irregularities and dislocations can significantly influence surface catalytic activity (4,39,42-44,53,56,62-64). Their presence as 'traps' can alter values of hydrogen diffusion coefficients (162), and they can markedly affect parameters such as internal friction (34) and the form of p-n relationships, particularly over the low content α phase range (94, 100).

Elastic and Anelastic Measurements

Ideas concerning the involvement of elastic interactions in phase transitions of metallic hydrides have continued to be developed (4, 11, 26, 95, 98, 104, 107, 108, 119-121, 124, 126, 134, 136, 163-167). These developments have been paralleled by studies of elastic constants and associated properties. Amplitudes and vibration frequencies of the palladium as well as hydrogen (deuterium) have been obtained by X-

ray and neutron scattering and by channelling (28,29, 118, 163-165, 168). This information has recently been combined with measurements of thermal expansions of both palladium hydrides and deuterides (33) for determinations of Grüneisen constants which are of interest in interpretations of superconductivity. Elastic constants in β phase palladium-hydrogen have been determined recently from measurements of ultrasonic sound velocities over a wide temperature range (32). These measurements confirmed earlier findings (4) of decreases of moduli with hydrogen content in the β phase. Also, as shown in Figure 8, the same trend has been found for recent measurements of Young's Modulus (34), calculated from changes of vibration frequencies and dimensions of palladium bars during studies of internal friction.

Gorsky Effect phenomena arising from time dependent long range migration of lattice dilating hydrogen under stress (51, 169-172), or related to strip-bending diffusion-elastic effects (58,173), have been extensively studied

as methods for measurements of hydrogen and deuterium diffusion coefficients.

With generally higher vibration frequencies and less thin specimens than those used (170) for observation of the Gorsky Effect, two further groups of peaks in plots of internal friction against temperature—which also have been attributed to stress induced relaxation processes associated with the presence of hydrogen in palladium and palladium alloys (34,40,97,98,174,175)—are seen.

One of these two groups of internal friction peaks has been related to a Zener type of relaxation effect (34,40,97,98) associated with stress-induced bulk lattice rearrangements of hydrogen interstitials and vacant interstitial sites. Figure 8 shows examples of the appearance of this Zener peak over the course of increasing and decreasing hydrogen content, and also illustrates corresponding plots of relaxation strength, related to the peak height, as a function of hydrogen content which have seemed to be diagnostic both of the Zener effect and of sequences of phase distributions (34). Asymmetries of the Zener peak and temperature dependences of relaxation strengths determined at different vibration frequencies have been

correlated with the anomalies in other properties near 50K (34). Studies of analogous Zener peaks found for palladium alloy-hydrogen systems are proving interesting (97,98,127,176) with reference to problems concerning trends in change of the hydrogen diffusion coefficient, phase relationships and states of lattice order near critical regions.

Towards the end of the absorption/desorption cycle, there is a prominent development of a further internal friction peak, illustrated in Figure 8, which has been associated with an interaction effect between hydrogen and the dislocations produced by the $\alpha = \beta$ transitions. Similar to the Zener peak, associated activation energies are compatible with a controlling hydrogen diffusion process (34). When previous distortions have already introduced dislocations, this hydrogen/dislocation peak appears significantly at extremely small hydrogen contents, to which certain nuclear magnetic and nuclear acoustic resonance effects also appear to be sensitive (177).

It is planned to conclude Dr. Lewis' review of the hydrogen-palladium system in the next issue of this journal.

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