

MLM-3159 (OP)

CONF. MLM--3659(OP)

COMPARISON OF HYDROGEN DIFFUSION IN  $Ti_2PdH_x$  TO

DE91 002711

THE BEHAVIOR FOR  $Ti_2CuH_x$  AND  $Zr_2PdH_x$

† R. C. Bowman, Jr.

Aerojet Electronic Systems Division

P. O. Box 296

Azusa, CA 91702 U.S.A.

A. Attalla and G. C. Abell

EG&G Mound Applied Technologies

P. O. Box 3000

Miamisburg, OH 45343 U.S.A.

J. S. Cantrell

Department of Chemistry

Miami University

Oxford, OH 45056 U.S.A.

and A. J. Maeland

Concrete Solutions

P. O. Box 1842

Meriden, CT 06450 U.S.A.

#### DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

1  
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

## SUMMARY

Nuclear magnetic resonance measurements of the proton spin-lattice and rotating-frame relaxation times were made on  $Ti_2PdH_x$  over the temperature range 100K to 580K. Analyses of the NMR data for  $Ti_2PdH_x$  gave hydrogen diffusion parameters that corresponded with the results previously obtained from  $Ti_2CuH_x$  and  $Zr_2PdH_x$  when the hydrogen atoms occupied a single type of tetrahedral interstitial site. However, the diffusion activation energy decreases in the sequence  $Ti_2PdH_{1.9}$ ,  $Ti_2CuH_{1.9}$ , and  $Zr_2PdH_{1.9}$ .

## INTRODUCTION

Several members of the  $A_2B$  intermetallic compound family with the tetragonal  $MoSi_2$ -type crystal structure can absorb hydrogen to produce ternary metal hydride phases [1,2]. Nuclear magnetic resonance (NMR) studies have been previously used to characterize the hydrogen diffusion behavior for  $Ti_2CuH_x$  [3] and  $Zr_2PdH_x$  [4,5]. Both host structure and hydrogen site occupancy were shown to influence the diffusion parameters. This paper reports NMR measurements of proton relaxation times for  $Ti_2PdH_x$  that reveal several similarities to the results for  $Ti_2CuH_x$  and  $Zr_2PdH_x$  as well as some interesting differences.

## SAMPLE DESCRIPTIONS AND EXPERIMENTAL PROCEDURES

$Ti_2PdH_x$  was prepared by reacting stoichiometric, arc-melted crystalline alloys with hydrogen gas at initial nominal pressures around one atmosphere. Heating up to 300-400°C was used to facilitate the reactions and the amount of hydrogen absorbed was calculated from differences between initial and final hydrogen pressure. The charged samples were handled in an argon dry box. Powders of  $Ti_2PdH_x$  for the NMR samples were loaded into 7mm o.d. glass tubes that were subsequently evacuated and flame sealed. After completion of the NMR experiments, phase compositions and structures were determined by powder x-ray diffraction which revealed the dominant hydride phase had the expected [1] orthorhombic distortion to the  $MoSi_2$  structure. However, the samples also had small amounts of a face-centered cubic (FCC) impurity phase believed to be  $Ti_4Pd_2O_y$  [6]. The measured lattice parameters for the orthorhombic  $Ti_2PdH_x$  and FCC phases are given in Table I. The reported stoichiometries were obtained by quantitative thermal desorption volumetric analyses on the remaining  $Ti_2PdH_x$  powder in the NMR samples.

A Bruker transient NMR spectrometer operating at a proton resonance frequency of 34.5 MHz was used to measure the spin-lattice ( $T_1$ ) and rotating-frame ( $T_{1\rho}$ ) relaxation times with standard pulse methods [3,4]. A spin-locking magnetic field of 7.3 G was applied during the  $T_{1\rho}$  measurements. The temperature range for the NMR experiments was from 100K to 580K. The magnetization recoveries during the  $T_1$  measurements were exponential as expected for protons in

a single phase host. However, the  $T_{1p}$  recoveries were usually nonexponential, which had been also observed for  $Ti_2CuH_x$  [3] and some  $Zr_2PdH_x$  samples. Consequently, the  $T_{1p}$  values reported for  $Ti_2PdH_x$  are defined as the time for the decay to reach  $1/e$  of its initial amplitude.

## RESULTS

The proton  $T_1$  relaxation times for transition metal hydrides can have three possible contributions [7]

$$T_1^{-1} = T_{1e}^{-1} + T_{1d}^{-1} + T_{1p}^{-1} \quad (1)$$

where  $T_{1e}$  arises from interactions with conduction electrons and  $T_{1e}^{-1} = C_K$ , the so-called Korringa constant that is related to the density of Fermi level electrons [7],  $T_{1d}$  is the dipolar modulation that is associated with various diffusion processes [7] in the solid, and  $T_{1p}$  is spin relaxation caused by paramagnetic impurities. The  $T_1$  data presented in Figure 1 for two  $Ti_2PdH_x$  revealed the temperature dependences expected when only the conduction electron mechanism contributes to  $T_1$  relaxation below room temperature. Consequently, paramagnetic relaxation is apparently negligible for these materials. The Korringa constants of 53.9 sK and 46.6 sK for  $Ti_2PdH_{1.47}$  and  $Ti_2PdH_{1.96}$ , respectively, are consistent with the values previously determined [3] for other Ti-based hydrides which imply similar electronic structures at the Fermi level [3,7].

The influence of hydrogen diffusion on the proton  $T_1$  and  $T_{1\rho}$  relaxation times for two  $Ti_2PdH_x$  samples is shown in Figure 2. The  $T_{1d}$  values were obtained by subtracting the appropriate  $T_{1e}$  terms from Figure 1. Although a  $T_{1d}$  minimum occurs near 550K for  $Ti_2PdH_{1.47}$  the  $T_{1d}$  minimum for  $Ti_2PdH_{1.96}$  was not reached by 580K, the maximum temperature obtainable with the present equipment. These results imply a faster hydrogen diffusion rate for  $Ti_2PdH_{1.47}$  which is consistent with the smaller activation energy ( $E_a$ ) of 0.40 eV from the  $T_{1d}$  data for this sample when compared to the 0.54 eV value obtained from  $Ti_2PdH_{1.96}$ . Furthermore, the minimum  $T_{1\rho}$  values are at 374K and 431K for  $Ti_2PdH_{1.47}$  and  $Ti_2PdH_{1.96}$ , respectively, which also indicates greater hydrogen mobility in the  $Ti_2PdH_{1.47}$  sample.

The well-known [7] BPP-model has been used to determine the diffusion hopping rates ( $\tau_c^{-1}$ ) from the  $T_{1d}$  and  $T_{1\rho}$  data when a minimum relaxation time was available. These parameters are summarized in Figure 3 where the straight lines are fits to the Arrhenius expression

$$\tau_c(T)^{-1} = \tau_0^{-1} \exp(-E_a/k_B T) \quad (2)$$

with the attempt frequency  $\tau_0^{-1}$  and Boltzmann's constant  $k_B$ . The  $E_a$  and  $\tau_0^{-1}$  values derived from the  $T_{1\rho}$  data are summarized in Table II. Although an unique  $E_a$  represents the  $T_{1d}$  and  $T_{1\rho}$  results for  $Ti_2PdH_{1.96}$ , the situation is more complicated for the  $Ti_2PdH_{1.47}$  sample where the two relaxation times yield different activation energies and the  $\tau_c^{-1}$  values from  $T_{1\rho}$  deviate significantly at lower temperatures from the Arrhenius line.

## DISCUSSION

The present proton NMR studies indicate that hydrogen diffusion in  $Ti_2PdH_x$  is qualitatively similar to that previously observed for  $Ti_2CuH_x$  [3] and  $Zr_2PdH_x$  [4,5] as well as for the face-centered-cubic binary hydrides  $TiH_x$  [8] and  $ZrH_x$  [9]. These results are not surprising since hydrogen occupies the same type of tetrahedral interstitial sites (i.e.,  $Ti_4$  or  $Zr_4$ ) in the ternary hydrides [10] with  $x < 2$  that are occupied in  $TiH_x$  or  $ZrH_x$ . However, the comparison of  $E_a$  from the BPP-model analyses of the  $T_{1\rho}$  relaxation times reveals in Table II that the activation energies are larger for the two  $Ti_2PdH_x$  samples. The reduction in symmetry from tetragonal to orthorhombic for the  $Ti_2PdH_x$  samples could lead to higher diffusion barriers. However, an alternative perspective arises from the fact that  $Ti_2PdH_2$  is the maximum composition whereas  $Ti_2CuH_3$  [3] and  $Zr_2PdH_{4.8}$  [10] can be produced. These greater stoichiometries for the latter hydrides require that additional interstitial sites to  $Ti_4$  or  $Zr_4$  must also be occupied. Consequently, the availability of these sites as intermediate positions in the diffusion process [3,7] could produce smaller barriers (i.e., lower  $E_a$ ) than are present in the binary hydrides. On the other hand, if such sites are energetically unfavorable in  $Ti_2PdH_x$  (as implied by a maximum hydrogen content of  $x=2$ ), they do not facilitate the diffusion jumps and an activation energy equal or larger than found in  $TiH_x$  (i.e.,  $E_a = 0.50$  eV according to Korn and Goren [8]) would result. This appears to be the situation found from the present proton NMR studies.

## ACKNOWLEDGMENTS

The authors thank R. W. Baker for the hydrogen desorption analyses. EG&G Mound Applied Technologies is operated for the U.S. Department of Energy under Contract No. DE-AC04-88DP43495.

## REFERENCES

1. R. Kadel and A. Weiss, Ber. Bunsenges. Physk. Chem. 82, 1290 (1978).
2. A. J. Maeland and G. G. Libowitz, J. Less-Common Met. 74, 295 (1980).
3. R. C. Bowman, Jr., A. J. Maeland, and W.-K. Rhim, Phys. Rev. B 26, 6362 (1982).
4. R. C. Bowman, Jr., A. Attalla, A. J. Maeland, and W. L. Johnson, Solid State Commun. 47, 779 (1983).
5. R. C. Bowman, Jr., D. R. Torgeson, R. G. Barnes, A. J. Maeland, and J. J. Rush, Z. Physk. Chem. N. F. 163, 425 (1989).
6. M. V. Nevitt, in Intermetallic Compounds, edited by J. H. Westbrook (Wiley, New York, 1967) p. 217.
7. R. C. Bowman, Jr., Hyperfine Interactions 24-26, 583 (1985).
8. C. Korn and S. D. Goren, Phys. Rev. B 22, 4727 (1980).
9. R. C. Bowman, Jr. and B. D. Craft, J. Phys. C: Solid State Phys. 17, L477 (1984).
10. F. E. Spada, R. C. Bowman, Jr., and J. S. Cantrell, J. Less-Common Met. 129, 197 (1984).

Table I. Lattice parameters from room temperature x-ray diffraction

<u>Material</u>	<u>Phase</u>	<u>a (nm)</u>	<u>b (nm)</u>	<u>c (nm)</u>
Ti <sub>2</sub> PdH <sub>1.47</sub>	Orthorhombic Hydride	0.3031(2)	0.3111(3)	1.111(6)
	FCC Impurity	1.207(2)	---	---
Ti <sub>2</sub> PdH <sub>1.96</sub>	Orthorhombic Hydride	0.3152(2)	0.2992(2)	1.137(1)
	FCC Impurity	1.245(9)	---	---

Table II. Comparison of hydrogen diffusion parameters derived from BPP-model analyses of proton T<sub>1ρ</sub> relaxation times

<u>Material</u>	<u>E<sub>a</sub>(eV)</u>	<u>τ<sub>0</sub><sup>-1</sup>(s<sup>-1</sup>)</u>	<u>Data Source</u>
Ti <sub>2</sub> PdH <sub>1.47</sub>	0.46±0.03	7.9x10 <sup>11</sup>	Present Work
Ti <sub>2</sub> PdH <sub>1.96</sub>	0.55±0.03	6.7x10 <sup>11</sup>	Present Work
Ti <sub>2</sub> CuH <sub>1.9</sub>	0.40±0.03	2.5x10 <sup>10</sup>	Bowman, et al. (1982)
Zr <sub>2</sub> PdH <sub>1.84</sub>	0.41±0.02	4.3x10 <sup>10</sup>	Bowman, et al. (1983)

FIGURE CAPTIONS

- Fig. 1 Proton spin-lattice relaxation times (T<sub>1</sub>) obtained below 300K.
- Fig. 2. Proton relaxation times for Ti<sub>2</sub>PdH<sub>1.47</sub> (a) and Ti<sub>2</sub>PdH<sub>1.96</sub> (b).
- Fig. 3. Temperature dependence of diffusion correlation times (τ<sub>c</sub>) and activation energies (E<sub>a</sub>) from BPP-model analyses of proton T<sub>1</sub> and T<sub>1ρ</sub> data for the Ti<sub>2</sub>PdH<sub>x</sub> samples.

FIGURE 1

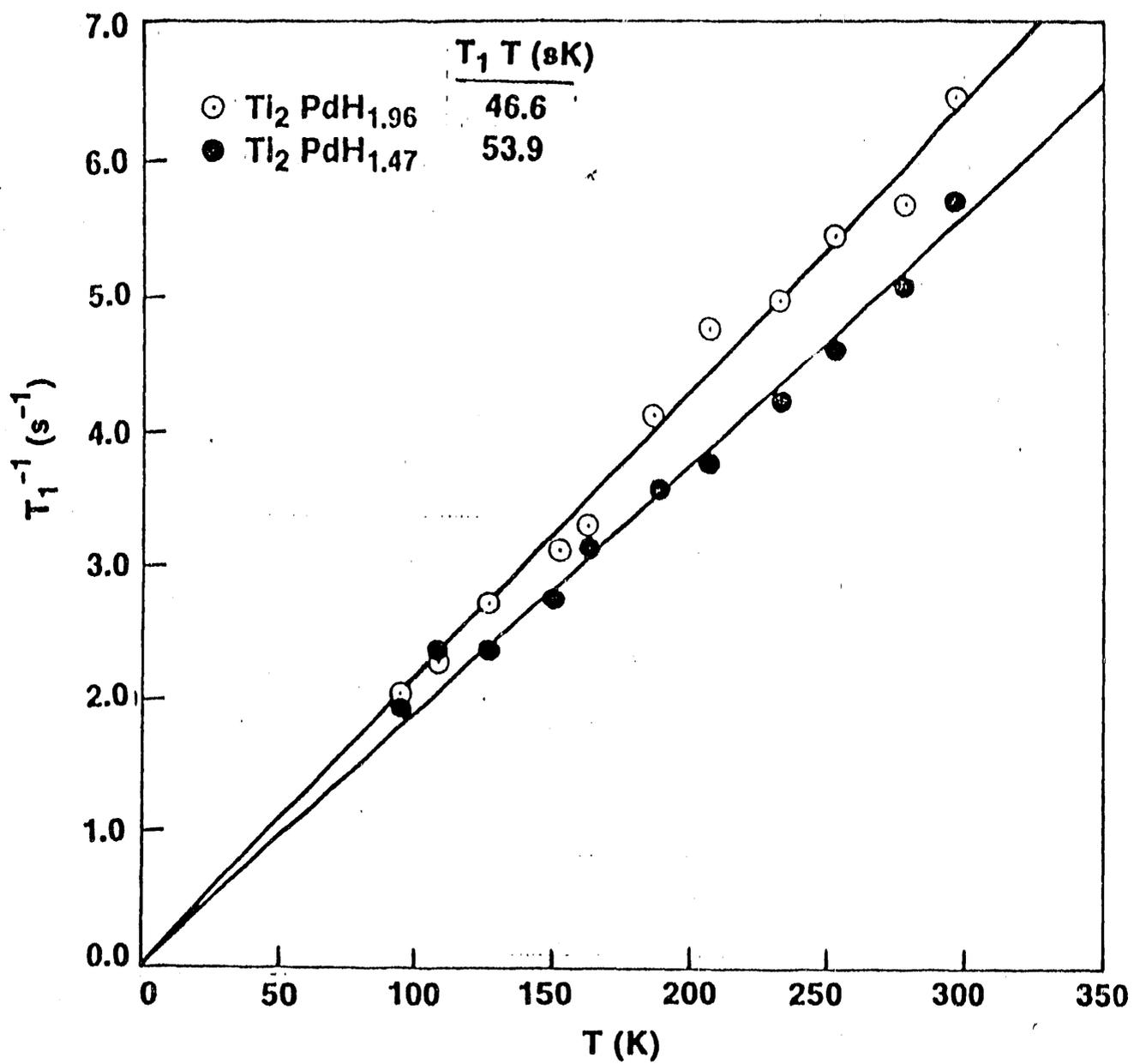


FIGURE 2

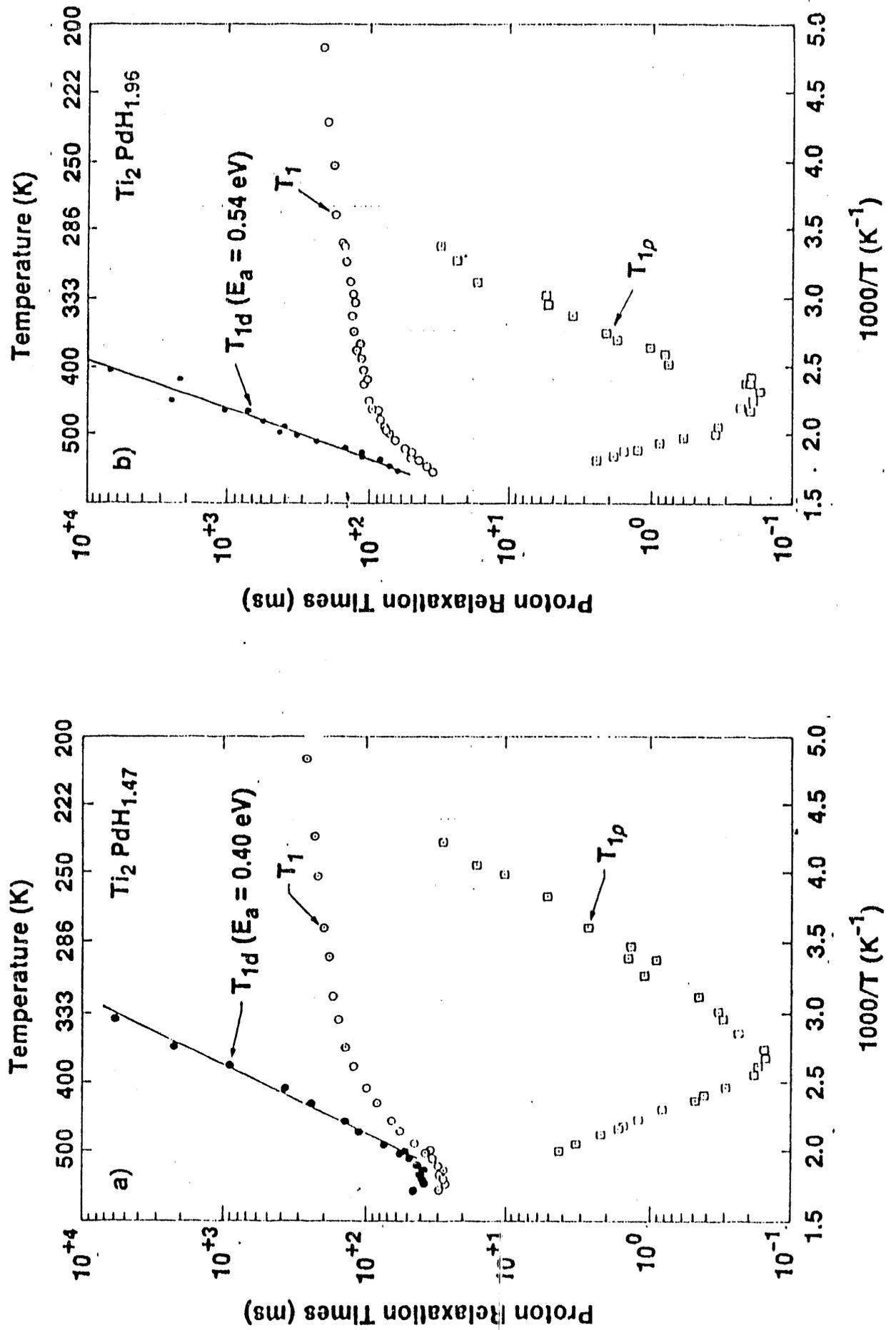
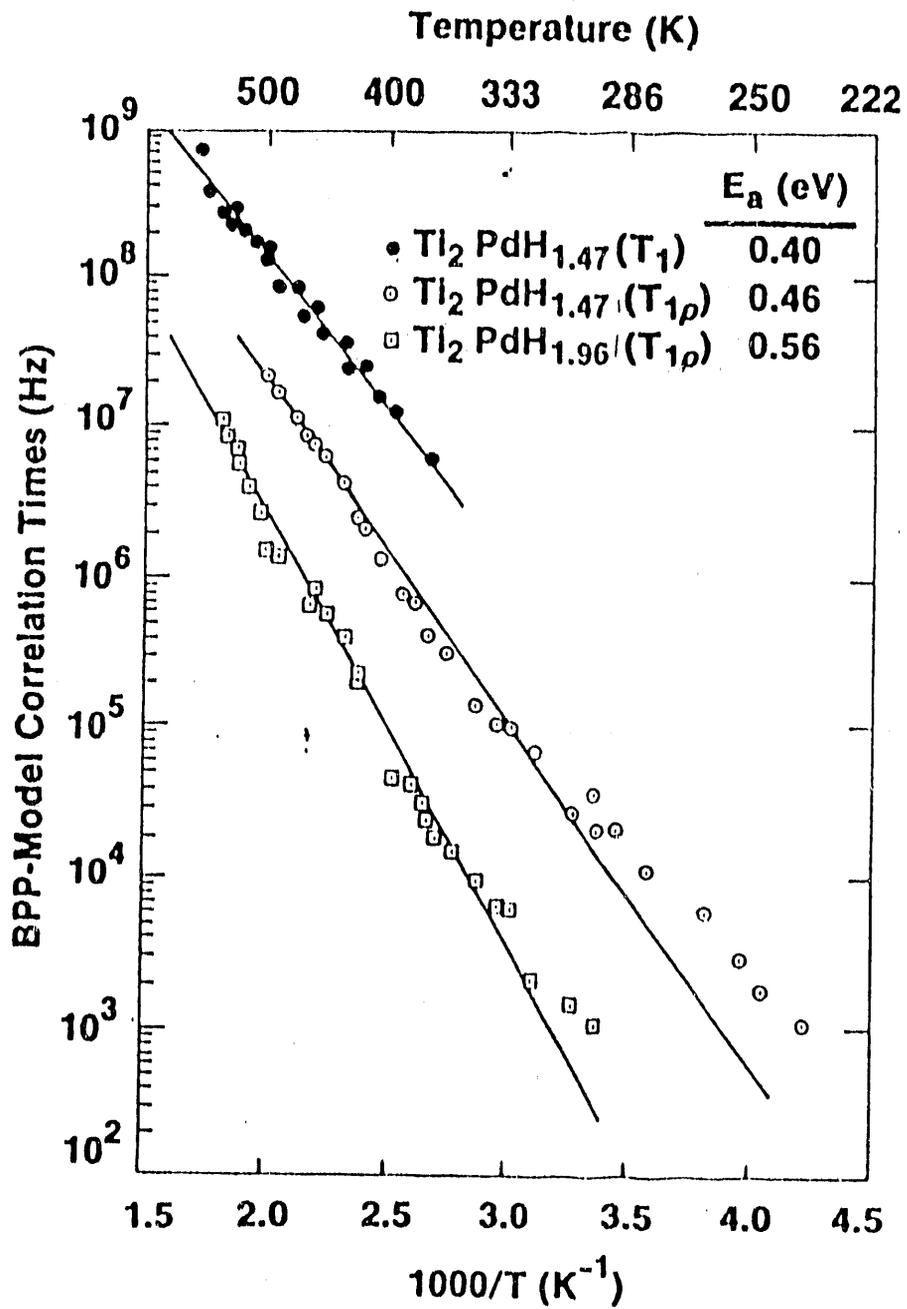


FIGURE 3



**END**

**DATE FILMED**

12 / 19 / 90