

## HYDROGEN DIFFUSION BEHAVIOR IN TITANIUM-CHROMIUM HYDRIDES WITH LAVES STRUCTURES

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## ABSTRACT

Extensive NMR measurements of the proton relaxation times have been performed on low (i.e.,  $\alpha$ -phase) and intermediate (i.e.,  $\alpha'$ -phase) hydrogen concentrations in  $\text{TiCr}_2\text{H}_x$  with both the hexagonal C14 and cubic C15 Laves structures. The relaxation times indicate rapid diffusion rates above 200 K for all the  $\text{TiCr}_2\text{H}_x$  phases; however, large differences in the diffusion activation energies are observed. This behavior is associated with the hydrogen interstitial site occupancies and diffusion pathways becoming restricted in the C14 structure.

## KEYWORDS

Metal Hydrides; Diffusion; Nuclear Magnetic Resonance; Hydrogen Storage; Laves-Structure Compounds; Proton Relaxation Times.

## INTRODUCTION

Many intermetallic compounds with the nominal stoichiometry  $\text{AB}_2$  have been found (Wernick, 1977) to possess C15 cubic (i.e., space group  $\text{Fd}3\text{m}$ ) or C14 hexagonal (i.e., space group  $\text{P}6_2/\text{mmc}$ ) Laves crystal structures. As described in the recent papers by Shaltiel (1978) and Jacob and Shaltiel (1979), many alloys with the C14 and C15 Laves structures will reversibly react with gaseous hydrogen to form ternary metal hydrides that often have rather large maximum storage capacities. Hence, several Laves alloys are very promising candidates for various hydrogen storage and energy conversion applications. Based upon relatively limited (but apparently representative) published data of Arita and others (1981), Pourarian and others (1981) and Fujii and others (1981), many  $\text{AB}_2$  alloys with either the C14 or C15 structure have good to excellent kinetics for both the absorption and desorption of hydrogen. Although the surface segregation of the  $\text{AB}_2$  alloys during hydriding produces (Pourarian and co-workers, 1981, Jacob and Polak, 1981) free B metal particles that may catalytically decompose  $\text{H}_2$  molecules at the alloy surface, a relatively rapid bulk hydrogen diffusion rate in the  $\text{AB}_2\text{H}_x$  phases is also an important factor in the favorable kinetics. In fact, recent nuclear magnetic measurements (NMR) of the proton relaxation times by Shinar and co-workers (1979, 1981) for the Laves hydrides  $\text{ZrMn}_2\text{H}_x$  (C14),  $\text{HfV}_2\text{H}_x$  (C15), and  $\text{ZrV}_2\text{H}_x$  (C15) indicate relatively high hydrogen diffusion rates with correspondingly low diffusion activation energies  $E_a$ . However, there has not been any previous comparative evaluation of the diffusion behavior between the C14 and C15 hydrides while retaining the same nominal ratio of identical metal atoms.

The present paper reports on proton NMR studies of the hydrogen diffusion behavior in both the C14 and C15 allotropes of nominal  $\text{TiCr}_2\text{H}_x$ . The  $\text{TiCr}_2$  alloys are particularly interesting since both the C15 and C14 structures have been shown by Johnson and Reilly (1978) and Johnson (1980) to form unstable hydride phases with rather large storage capacities that make these alloys suitable for applications involving temperatures well below ambient. The proton relaxation times indicate rapid diffusion rates above 200 K for the low (i.e.,  $\alpha$ -phase) and intermediate (i.e.,  $\alpha'$ -phase) hydrogen concentrations in both the C14 and C15 structures of  $\text{TiCr}_2\text{H}_x$ ; however, the diffusion behavior is complex with non-Arrhenius temperature dependences as well as evidence for simultaneous slow and rapid motion processes below 170 K. Above 200 K the  $E_a$  values for the C14 and C15  $\alpha$ -phase samples are nearly identical while a large difference exists between the  $\alpha'$ -phase samples. This behavior can be qualitatively associated with differences in hydrogen site occupancies and more restricted diffusion pathways in the C14 Laves structure.

#### EXPERIMENTAL SECTION

Extensive descriptions of the preparative procedures for the  $\text{TiCr}_2\text{H}_x$  alloys with the C15 and C14 structures as well as thermodynamic quantities and tentative phase diagrams have been previously given by Johnson and Reilly (1978) and Johnson (1980) and, thus, only a brief summary of sample preparation will be given. The C15 Laves hydrides were prepared from a single-phase alloy of composition  $\text{TiCr}_{1.8}$  while the C14 hydrides were from a single-phase alloy with the composition  $\text{TiCr}_{1.9}$ . Recent unpublished diffraction and density data from Brookhaven National Laboratory indicate the nonstoichiometry of the  $\text{TiCr}_y$  alloys corresponds to substitutional disorder where some Ti-atoms occupy Cr lattice positions of the ideal C15 and C14 Laves structures. It has not been possible to prepare single phase alloys with the stoichiometric composition  $\text{TiCr}_{2.0}$ . The NMR samples of both the low hydrogen content (i.e.,  $\alpha$ -phase or solid solution) and the intermediate hydrogen content (i.e.,  $\alpha'$ -phase) were prepared by direct reaction with  $\text{H}_2$  gas in the single-phase regions of the C15 ( $\text{TiCr}_{1.8}\text{-H}$ ) and C14 ( $\text{TiCr}_{1.9}\text{-H}$ ) phase diagrams. Because the  $\text{TiCr}_y\text{H}_x$  samples will spontaneously decompose at ambient temperature or even much lower temperatures due to the combined effect of high dissociation pressures and rapid desorption kinetics, it was necessary to stabilize (Johnson and Reilly, 1978) the  $\text{TiCr}_y\text{H}_x$  powders by exposure to high-pressure CO at low temperatures before removing the hydride products from the synthesis reactor. The CO forms a surface film on the  $\text{TiCr}_y\text{H}_x$  particles that greatly inhibits the loss of hydrogen from the interior. Portions of the CO-stabilized  $\text{TiCr}_y\text{H}_x$  were subsequently sealed in evacuated 7 mm-o.d. pyrex NMR sample tubes. To prevent accidental decomposition these samples were never heated above 300 K. The reported compositions of the  $\text{TiCr}_y\text{H}_x$  samples were determined by volumetric analyses following completion of the NMR experiments.

Conventional pulse techniques were used to measure the various proton relaxation times over the temperature range 100 K to 300 K. The inversion-recovery sequence yielded the spin-lattice relaxation times  $T_1$  while the phase-shifted rf pulse method with an applied magnetic field of 7.3 Gauss was used to determine  $T_{1\rho}$ , the spin-lattice relaxation time in the rotating frame. The simple two-pulse spin-echo sequence gave the  $T_2'$  values. The spin-spin relaxation times  $T_{2m}$  were determined using the CPMG sequence of Carr and Purcell (1954) and Meiboom and Gill (1958) with a spacing of 200  $\mu\text{s}$  between the  $\pi$ -pulses. All the measurements were performed at a proton resonance frequency of 34.5 MHz on a NMR spectrometer previously described by Bowman, Attalla, and Maeland (1978).

#### RESULTS

The proton relaxation times for the four CO-stabilized  $\text{TiCr}_y\text{H}_x$  samples are summarized in Figs. 1-4.  $\text{TiCr}_{1.8}\text{H}_{0.55}$  ( $\alpha$ -phase) and  $\text{TiCr}_{1.8}\text{H}_{2.58}$  ( $\alpha'$ -phase) have the cubic C15 structure while  $\text{TiCr}_{1.9}\text{H}_{0.63}$  ( $\alpha$ -phase) and  $\text{TiCr}_{1.9}\text{H}_{2.85}$  ( $\alpha'$ -phase) have the hexagonal C14 structure. From the general relationships between nuclear relaxation times

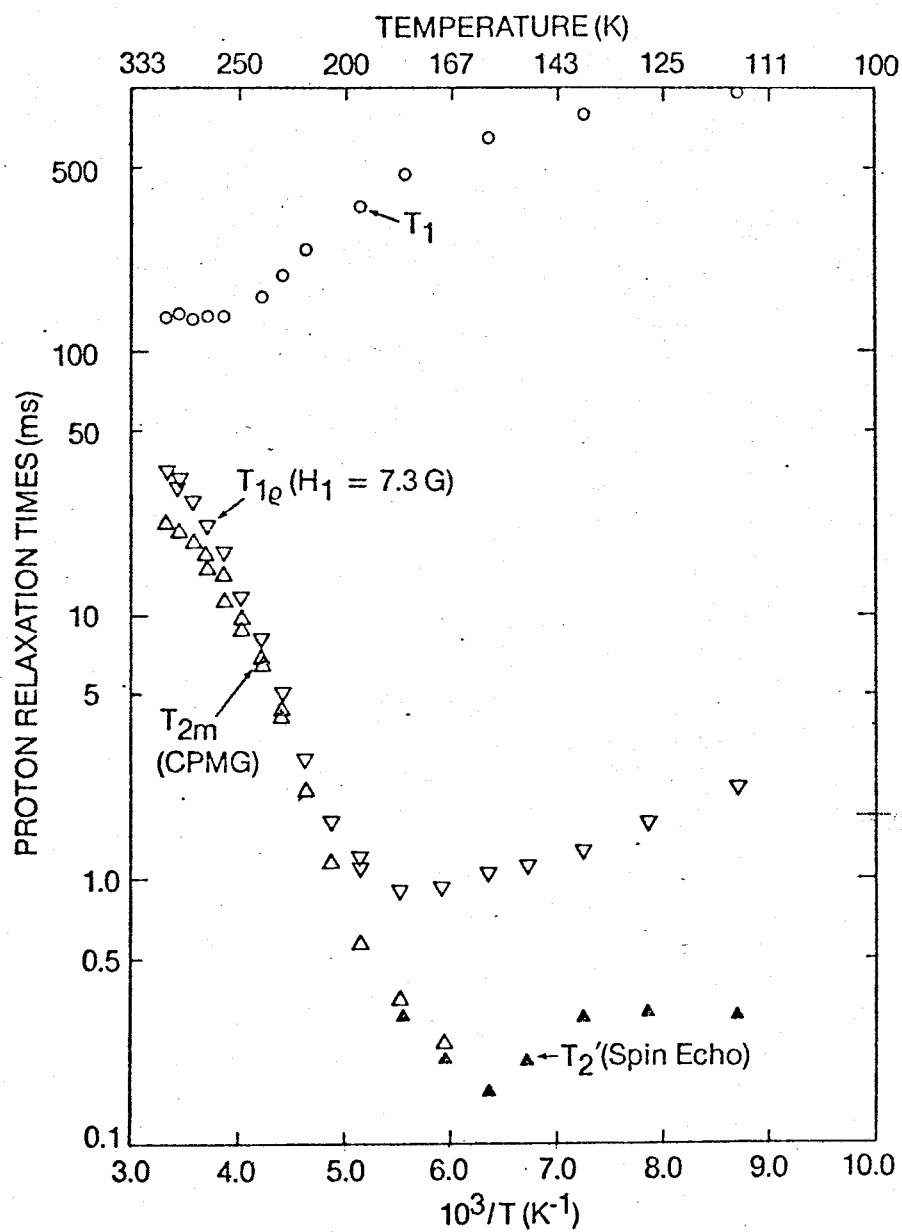


Fig. 1. The proton relaxation times  $T_1$ ,  $T_{1\rho}$ ,  $T_2'$ , and  $T_{2m}$  for CO-stabilized  $\alpha$ -phase  $\text{TiCr}_{1.8}\text{H}_{0.55}$  with the C15 Laves structure.

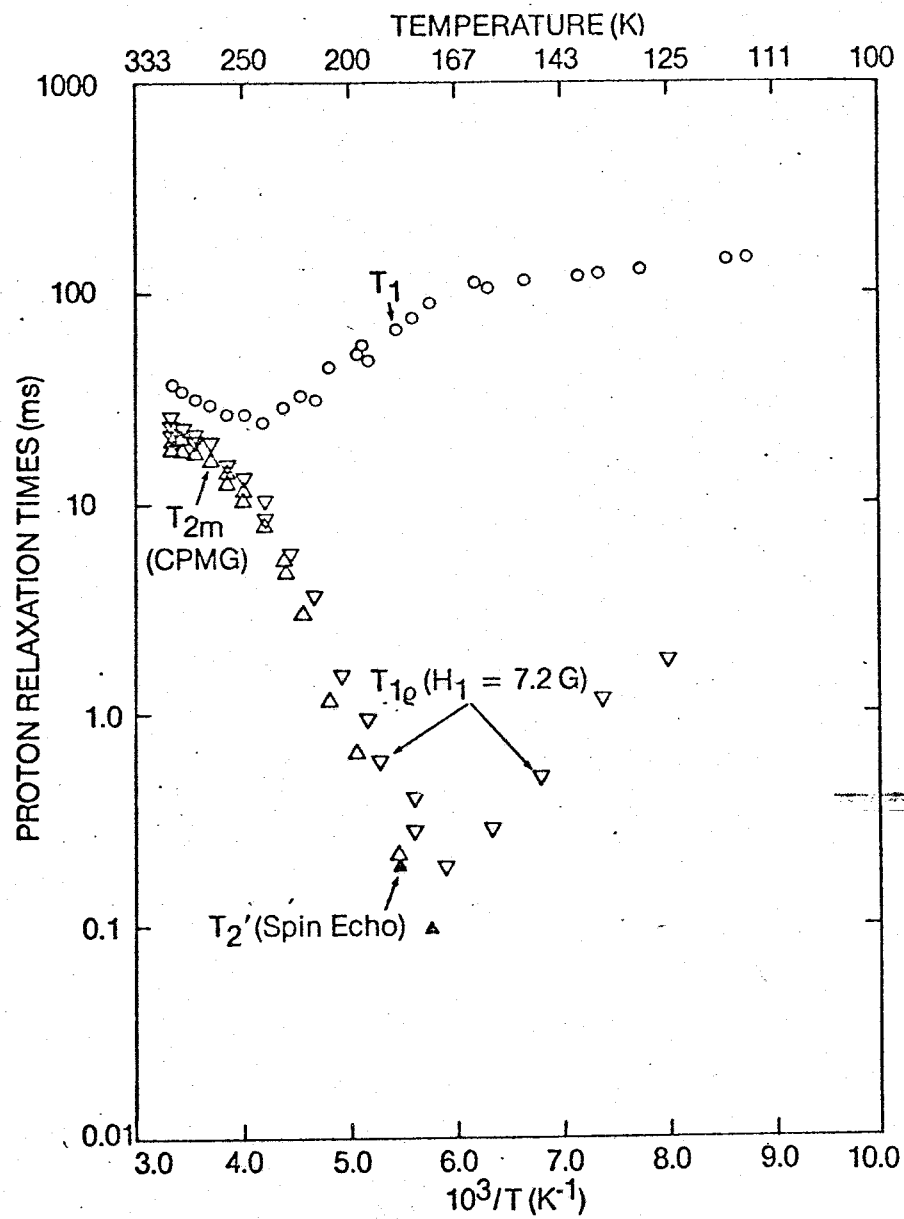


Fig. 2. The proton relaxation times  $T_1$ ,  $T_{1\rho}$ ,  $T_2'$ , and  $T_{2m}$  for CO-stabilized  $\alpha'$ -phase  $\text{TiCr}_{1.8}\text{H}_{2.58}$  with the C15 Laves structure.

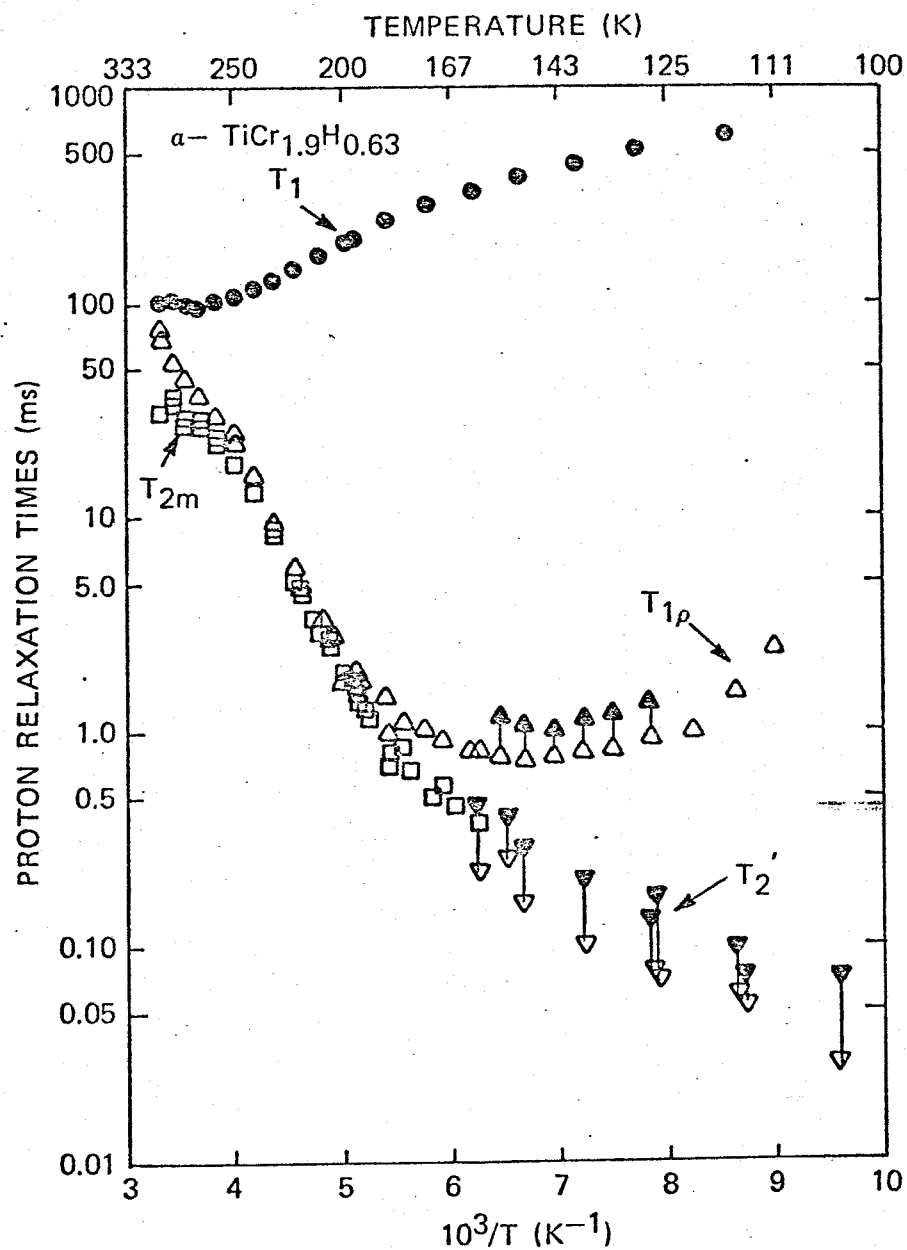


Fig. 3. The proton relaxation times  $T_1$ ,  $T_{1\rho}$ ,  $T_2$ , and  $T_{2m}$  for CO-stabilized  $\alpha$ -phase  $\text{TiCr}_{1.9}\text{H}_{0.63}$  with the C14 Laves structure. The short vertical lines connect limiting  $T_{1\rho}$  and  $T_2$  values in regions of nonexponential recovery.

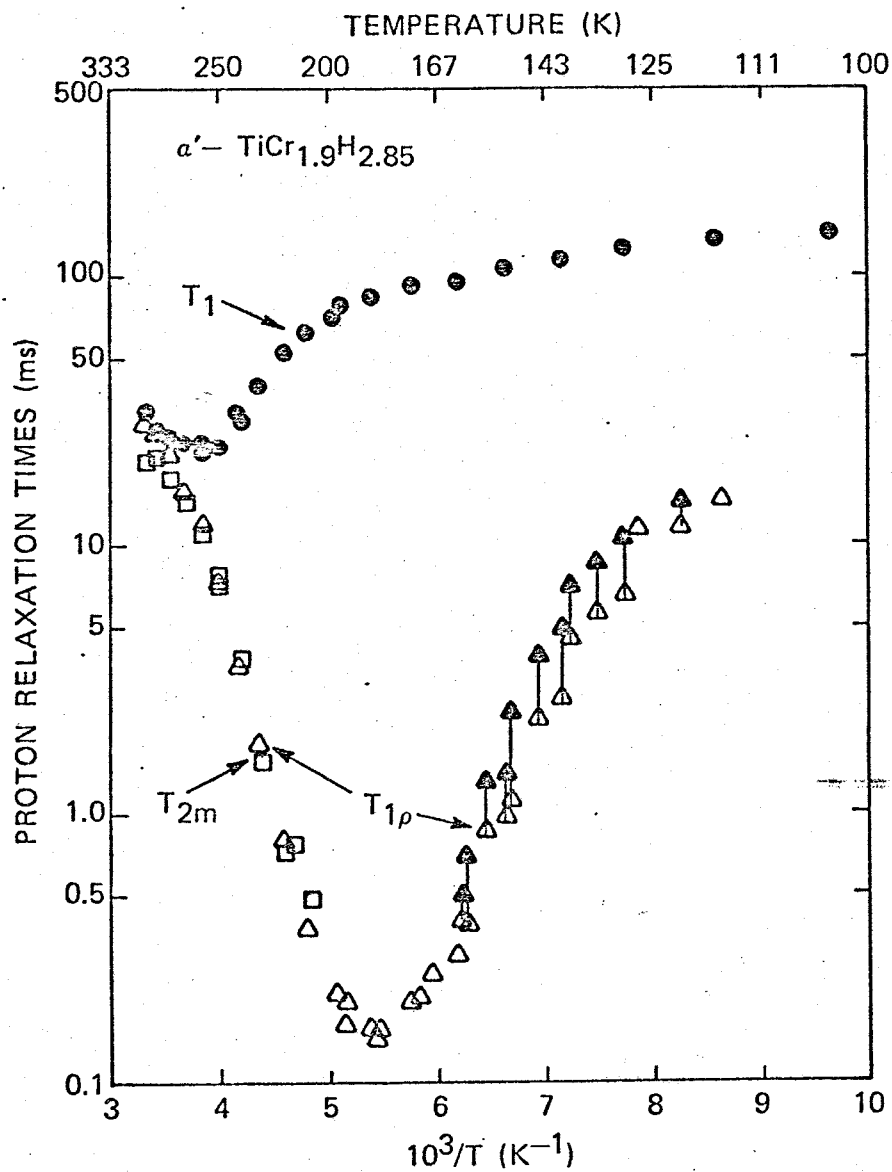


Fig. 4. The proton relaxation times  $T_1$ ,  $T_{1\rho}$ , and  $T_{2m}$  for CO-stabilized  $\alpha'$ -phase  $\text{TiCr}_{1.9}\text{H}_{2.85}$  with the C14 Laves structure. The short vertical lines connect limiting  $T_{1\rho}$  values in a region of nonexponential recovery.

and the hydrogen diffusion rate that have been thoroughly described by Cottis (1972, 1978), the data in Figs. 1-4 indicate substantial hydrogen mobility is characteristic of both the Cl4 and Cl5 TiCr<sub>y</sub>H<sub>x</sub> phases. The specific evidence for rapid hydrogen diffusion includes the following: 1) the T<sub>1</sub> minima, which correspond (Cottis, 1972, 1978) to a mean H-atom hopping rate of approximately  $2 \times 10^8 \text{ sec}^{-1}$ , occur at temperatures between 240 K and 260 K; 2) the T<sub>1ρ</sub> minima, which correspond to a hopping rate of about  $2 \times 10^6 \text{ sec}^{-1}$ , occur in the temperature range 140 K to 170 K; and 3) the observed T<sub>2</sub> values from both the CPMG and spin echo techniques exceed the predicted dipolar rigid-lattice values to temperatures below 160 K for the α'-samples and to nearly 100 K for the α-phase samples. Combining these observations provides an unmistakable case of high hydrogen mobility as has been found by Shinar and co-workers (1979, 1981) in other Cl4 and Cl5 hydrides. Before proceeding to the quantitative analyses of the proton relaxation times, some unusual aspects of the data in Figs. 1-4 should be noted. First, the relaxation times T<sub>1ρ</sub> and T<sub>2</sub>' for the Cl4 TiCr<sub>1.9</sub>H<sub>x</sub> samples are nonexponential below 160 K. Similar behavior has been observed in β-LaNi<sub>5</sub>H<sub>7</sub> (Karliceck and Lowe, 1980, Chang, Lowe, and Karliceck, 1981) and β-LaNi<sub>5-y</sub>Al<sub>y</sub>H<sub>x</sub> (Bowman and co-workers, 1980) and is attributed to the simultaneous motion of inequivalent H-atoms with different hopping rates. The minimum in T<sub>2</sub>' for α-TiCr<sub>1.8</sub>H<sub>0.55</sub> (see Fig. 1) is probably caused by an atomic exchange process (Goldman and Shen, 1966) between mobile and locally trapped H-atoms. The substitutionally disordered Ti atoms that occupy Cr positions are believed to be the trapping sites. This mechanism is currently under experimental study and will be described in more detail elsewhere.

Translational diffusion of H-atoms affect proton relaxation times through a time-dependent modulation of the dipolar interactions (Cottis, 1972, 1978). Since the <sup>47</sup>Ti, <sup>49</sup>Ti, and <sup>53</sup>Cr magnetic nuclei have small moments and low isotopic abundances, only the proton-proton dipolar interactions need be considered. However, the relaxation times in Figs. 1-4 require some corrections to remove the non-diffusion contributions. For example, T<sub>1</sub> in metallic systems will generally obey the relation:

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

where T<sub>1d</sub> is the diffusion contribution (Cottis, 1972, 1978) and T<sub>1e</sub> arises from hyperfine interactions with the conduction electrons. The T<sub>1e</sub> term is easily determined (Bowman and others, 1980) from the temperature dependence of T<sub>1</sub> at low temperatures where the T<sub>1d</sub> contribution becomes insignificant (Cottis, 1978). Similar corrections are usually required (Bowman and others, 1980) for the T<sub>2m</sub> and T<sub>1ρ</sub> parameters as well. For rather general conditions (Cottis, 1978), these corrected proton relaxation times can be related to the diffusion correlation time τ<sub>c</sub> through the expressions (Bowman and others, 1978, 1980):

$$T_{1d}^{-1} = C_1 \tau_c^{-1} \quad (\text{below the } T_1 \text{ minimum}) \quad (2)$$

$$T_{1\rho}^{-1} = C_2 \tau_c / (1 + 4 \omega_1^2 \tau_c^2) \quad (3)$$

$$T_{2d}^{-1} = C_3 \tau_c \quad (4)$$

where C<sub>i</sub> (i = 1, 2, 3) are model-dependent constants (Cottis, 1978) and ω<sub>1</sub> is the angular frequency of the spin-locking field H<sub>1</sub>. Since τ<sub>c</sub> is inversely proportional (Cottis, 1972, 1978) to the hydrogen diffusion constant D, the E<sub>a</sub> values may be derived from the temperature dependence of the relaxation times given in eqns. (2)-(4) by assuming τ<sub>c</sub> obeys the Arrhenius relation:

$$\tau_c = \tau_{c\infty} \exp(E_a/k_B T) \quad (5)$$

where τ<sub>c∞</sub> is the inverse of the attempt frequency and k<sub>B</sub> is the Boltzmann's factor.

The  $E_a$  values that were obtained from the corrected proton relaxation times for the four  $\text{TiCr}_y\text{H}_x$  samples are summarized in Table 1. It is immediately obvious that in each sample unique  $E_a$  values were not obtained from the different relaxation times. Although the  $T_{2d}$  and  $T_{1\rho}$  data for temperatures above the  $T_{1\rho}$  minima give nearly identical  $E_a$  values, the  $T_{1d}$ ,  $T_2'$ , and low-temperature  $T_{1\rho}$  data yield significantly smaller  $E_a$  values. Similar behavior has recently been seen in several other metal hydrides including  $\beta\text{-LaNi}_5\text{H}_7$  (Karlicek and Lowe, 1980) and  $\beta\text{-LaNi}_{5-y}\text{Al}_y\text{H}_x$  (Bowman and co-workers, 1980). It has been suggested by Karlicek and Lowe (1980) and Bowman and co-workers (1980) that the various NMR relaxation times can respond differently to two types of motion. The smaller  $E_a$  values represent local hopping among closely spaced interstitial H-sites while the larger  $E_a$  values correspond to jump processes involved in long-range diffusion. The role of structure on this complex and currently incompletely developed diffusion mechanism will be briefly considered for the C14 and C15  $\text{TiCr}_y$  hydrides in the next section.

TABLE 1 Comparison of Activation Energies  $E_a$  from Proton NMR Measurements for  $\text{TiCr}_2\text{H}_x$  Samples with the C14 and C15 Laves Crystal Structures.

Sample Composition	Laves Structure Type	NMR Parameter	Temperature Range (K)	$E_a$ (eV)
$\text{TiCr}_{1.8}\text{H}_{0.55}$	C15 ( $\alpha$ )	$T_{1d}$	180-250	$0.13 \pm 0.01$
		$T_{1\rho}$	190-280	$0.19 \pm 0.02$
		$T_{1\rho}$	115-170	$0.03 \pm 0.01$
		$T_{2d}$	180-260	$0.20 \pm 0.01$
$\text{TiCr}_{1.8}\text{H}_{2.58}$	C15 ( $\alpha'$ )	$T_{1d}$	180-240	$0.135 \pm 0.01$
		$T_{1\rho}$	180-280	$0.25 \pm 0.02$
		$T_{1\rho}$	120-170	$0.10 \pm 0.01$
		$T_{2d}$	180-250	$0.26 \pm 0.01$
$\text{TiCr}_{1.9}\text{H}_{0.63}$	C14 ( $\alpha$ )	$T_{1d}$	170-250	$0.088 \pm 0.010$
		$T_{1\rho}$	180-290	$0.218 \pm 0.010$
		$T_{2d}$	180-260	$0.205 \pm 0.010$
		$T_2'$	105-170	$0.050 \pm 0.005$
$\text{TiCr}_{1.9}\text{H}_{2.85}$	C14 ( $\alpha'$ )	$T_{1d}$	200-250	$0.28 \pm 0.01$
		$T_{1\rho}$	200-270	$0.40 \pm 0.02$
		$T_{1\rho}$	125-175	$0.18 \pm 0.02$
		$T_{2d}$	200-270	$0.40 \pm 0.02$

#### DISCUSSION

In both the C14 and C15 Laves structures for  $\text{AB}_2$  alloys the only interstitial lattice sites that are available (Magee, Liu, and Lundin, 1981) for occupancy by the hydrogen atoms have distorted tetrahedral symmetry with  $\text{A}_2\text{B}_2$ ,  $\text{AB}_3$ , or  $\text{B}_4$  as the nearest neighbor coordination. The recent calculations by Magee, Liu, and Lundin (1981) have demonstrated that  $\text{A}_2\text{B}_2$  sites have the largest radii for both C15 and C14 structures. On the premise that H-atoms preferentially occupy the largest available sites



amenable with formation of reasonable metal-hydrogen bonds, it is expected that the  $A_2B_2$  sites would be more readily occupied. Furthermore, since chromium can only form a hydride phase with difficulty while  $TiH_2$  is a prototype stable transition metal hydride, the  $TiCr_3$  and  $Cr_4$  sites are unlikely to be significantly occupied. This view is in complete agreement with neutron diffraction studies of the Cl5 deuterides  $ZrCr_2D_x$  ( $x = 2.89$  and  $3.08$ ) by Fruchart and co-workers (1980),  $ZrCr_2D_{3.5}$  by Yartys' and co-workers (1980) and  $TiCr_{1.8}D_x$  ( $x = 0.85$  and  $2.20$ ) by Reidinger and co-workers (unpublished results) where the best fits to all the powder patterns indicated only  $Zr_2Cr_2$  or  $Ti_2Cr_2$  sites contained deuterium. Although neutron diffraction data are not currently available for  $ZrCr_2D_x$  or  $TiCr_2D_x$  with the Cl4 structure, Didisheim and co-workers (1979) found the D-atoms to occupy only  $Zr_2Mn_2$  sites in the Cl4 phase  $ZrMn_2D_3$ . Although all the  $A_2B_2$  sites are equivalent in the Cl5 structure (i.e., subgroup 96g), there are four distinct  $A_2B_2$  sites existing for the Cl4 structure (i.e., subgroups 6h,  $6h_2$ ,  $12k$ , and  $24l$ ). From a consideration of the arrangements (Magee, Liu, and Lundin, 1981, Didisheim and co-workers, 1979) of the  $A_2B_2$  sites in the Cl4 and Cl5 structures, it is clear that H-atom hopping paths involving only equivalent sites in the Cl5 structure will include two or more different sites for the Cl4 phase. This inequivalency among the  $A_2B_2$  sites for the Cl4 structure may account for the nonuniform occupancy of deuterium atoms in the several  $Zr_2Mn_2$  sites that has been found in  $ZrMn_2D_3$  by Didisheim and co-workers (1979).

An examination of the  $E_a$  parameters in Table 1, which summarize the hydrogen diffusion behavior in  $TiCr_yH_x$  ( $y = 1.8$  and  $1.9$ ) as represented by the proton relaxation time data given in Figs. 1-4, illustrates that host metal structure appears to play a major role for the diffusion processes in the Cl5 and Cl4 Laves phases. This assertion is most exemplified from a comparison of the  $E_a$  parameters above 180 K for  $\alpha'$ - $TiCr_{1.9}H_{2.85}$  (Cl4) with the  $E_a$  values for  $\alpha$ - $TiCr_{1.9}H_{0.63}$  (Cl4) and  $\alpha'$ - $TiCr_{1.8}H_{2.58}$  (Cl5). In the Cl5 structure  $E_a$  increased by  $\leq 20\%$  in going from  $\alpha$  to  $\alpha'$  phase. This increase may correspond to correlation effects (Mauger, Williams, and Cotts, 1981) in the H-atom jumps at the larger hydrogen concentration. However,  $E_a$  increases by a factor of two between the  $\alpha$ - $TiCr_{1.9}H_{0.63}$  and  $\alpha'$ - $TiCr_{1.9}H_{2.85}$  samples. Furthermore, the  $E_a$  parameter is significantly smaller in Cl5  $\alpha'$ - $Ti_{1.8}H_{2.58}$  compared to that for the Cl4  $\alpha'$ -sample. The much larger  $E_a$  value for the Cl4  $\alpha'$ -phase sample must reflect a higher barrier to hydrogen diffusion compared to those pathways that are available to H-atoms in either the  $\alpha$ -phase or the  $\alpha'$ -phase with Cl5 structure. Since the  $E_a$  values are similar for  $\alpha$ -phase samples with either Cl4 or Cl5 structure, the reduction in symmetry from cubic to hexagonal cannot be directly responsible for a large  $E_a$  increase. It is possible that preferential ordering of H-atoms on a portion of the inequivalent  $Ti_2Cr_2$  sites in the Cl4 structure can occur above a minimum H-atom concentration. If some of these H-atoms occupy sites corresponding to deeply bound potential well minima that also block the more accessible diffusion pathways (Didisheim and co-workers, 1979), diffusion would necessarily proceed along alternative paths with larger  $E_a$  requirements. However, from analysis of proton  $T_2$  relaxation times for  $ZrMn_2H_x$  ( $2.0 \leq x \leq 3.4$ ) with the Cl4 structure, Shinar and co-workers (1979) obtained  $E_a = 0.16 \pm 0.03$  eV, which is apparently independent of hydrogen concentration. Hence, the restricted diffusion process suggested for  $\alpha'$ - $TiCr_{1.9}H_{2.85}$  does not appear applicable for isostructural  $ZrMn_2H_x$ .

Before a more comprehensive description of diffusion in the  $TiCr_2H_x$  phases can be developed, further information on the low-temperature interstitial site occupancies should be obtained by neutron diffraction measurements on Cl4 and Cl5  $TiCr_2D_x$  to determine the distribution of D-atoms among the  $Ti_2Cr_2$  sites. The contributions of the Ti-Cr substitutional disorder to the hydrogen diffusion mechanisms also need clarification. Extension of the proton relaxation time measurements to other  $AB_2H_x$  systems which can be prepared in the Cl4 and Cl5 forms would be valuable.

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