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NMR studies of diffusion in the metallic glass $TiCuH_x$

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Proton relaxation times have been measured in the glassy hydride a-$TiCuH_x$ for $1.27 \leq x \leq 1.35$ over the temperature range 100 to 430 K. Analyses of the proton T_2 and T_{1D} relaxation times indicate that hydrogen mobility in amorphous $TiCuH_{1.3}$ is significantly greater than in crystalline $TiCuH_{0.94}$ or fcc γ-TiH_x. Furthermore, a-$TiCuH_x$ exhibits non-Arrhenius behavior with four different diffusion activation energies being obtained, whereas diffusion in both $TiCuH_{0.94}$ and γ-TiH_x can be represented by single activation energies over wide temperature ranges. These results demonstrate that local structure plays a major role in the diffusion mechanisms in both the crystalline and amorphous hydride phases. A partial, but irreversible, decomposition of the a-$TiCuH_x$ phase was also observed near 420 K.

I. INTRODUCTION

Two of the most active research areas involving metals are the properties of amorphous alloys and the behavior of hydrogen in metals. Since the specific roles of local structure on diffusion mechanisms remain poorly understood for both amorphous alloys[1] and metal-hydrogen systems,[2] comparisons of hydrogen diffusion in crystalline and amorphous metal hydride phases could provide useful insights on the relationship between structure and diffusion. Metallic glasses form readily in the $Ti_{1-y}Cu_y$ system over the wide composition range of 30–70 at.% Cu which includes the crystalline intermetallic compounds TiCu and Ti_2Cu. Both TiCu and Ti_2Cu have been found[3,4] to form ternary hydrides with limiting compositions $TiCuH_{1.0}$ and $Ti_2CuH_{2.8}$. Under suitable conditions the corresponding $Ti_{1-y}Cu_y$ glasses can also absorb hydrogen without crystallization[3,4] to form amorphous hydrides such as a-$TiCuH_x$ where $1.2 < x < 1.35$.

A previous nuclear-magnetic-resonance (NMR) study[5] has shown that structure is very important to hydrogen diffusion in crystalline $TiCuH_{0.94}$. The TiCuH crystal structure consists of alternating layers of TiH_2 and Cu which produces a two-dimensional analog of the fcc γ-TiH_2 structure. Neutron-diffraction measurements[6] of TiCuD indicate a nearly ideal tetrahedral coordination of Ti atoms about each D atom with Ti–Ti, Ti–D, and D–D interatomic distances almost identical to those in γ-TiD_2. Because a double layer of Cu atoms separates each TiH_x layer, diffusion in crystalline $TiCuH_x$ is restricted to jumps between nearest-neighbor tetrahedral sites within the H-atom plane while jumps through vacant octahedral sites are possible[7] in fcc γ-TiH_x. In fact, theoretical studies[8] of diffusion in γ-TiH_2 predict that H atom jumps through the octahedral sites have smaller activation energies (E_a) than direct jumps between neighboring tetrahedral sites. These predictions are supported by the proton NMR measurements[5] on $TiCuH_{0.94}$ which yielded $E_a = 0.8$ eV and is 0.3 eV larger than E_a obtained in γ-TiH_x.[7,9]

The present paper describes similar NMR studies of hydrogen diffusion behavior in amorphous a-$TiCuH_x$. The proton relaxation times for a-$TiCuH_x$ indicate a much more rapid diffusion rate than is observed in crystalline $TiCuH_{0.94}$ (Ref. 5) and TiH_x.[9] The more varied local structures in a-$TiCuH_x$ appear to favor a greatly enhanced H-atom mobility when compared to the structurally allowed diffusion mechanisms in $TiCuH_{0.94}$ and γ-TiH_x. Although diffusion in both $TiCuH_{0.94}$ and TiH_x exhibit Arrhenius temperature dependence over wide temperature ranges,[5,7,9] several E_a values are needed to represent hydrogen diffusion in a-$TiCuH_x$. This behavior is entirely consistent with the variation in local structure about the H atoms that has been suggested by the recent inelastic neutron scattering spectra[10] of a-$TiCuH_{1.3}$.

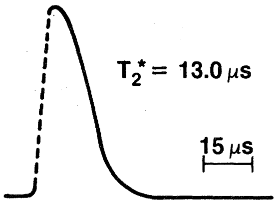
II. EXPERIMENTAL DETAILS

The metallic glass TiCu samples were in the form of vacuum cast ribbons. Hydrogen absorption from the gas phase was performed at room temperature to avoid crystallization and the reaction generally required several days for completion. X-ray-diffraction patterns of the a-$TiCuH_x$ samples gave the broad maxima that are characteristic[11] of amorphous solids and verified that no crystallization had occurred during the hydriding process. Further information on the preparation and properties of a-TiCuH$_x$ has been published elsewhere.[3,4,10] The a-TiCuH$_x$ samples were very brittle, in contrast to the quite ductile amorphous TiCu, and were readily crushed into fine powder prior to loading into 7-mm o.d. NMR sample tubes, which were subsequently evacuated and sealed. All the samples were handled and kept in an argon dry box. The compositions of the NMR-investigated a-TiCuH$_x$ samples ranged between $1.27 \leq x \leq 1.35$ using the volumetric measurements[4] during synthesis. The proton spin-lattice (T_1), dipolar[12] (T_{1D}), line-shape (T_2^*), spin-echo (T_2'), and Carr-Purcell-Meiboom-Gill[13] (CPMG) spin-spin (T_{2m}) relaxation times were measured at a resonance frequency of 34.5 MHz using equipment and procedures previously described.[5] At temperatures below the onset of an irreversible decomposition[3,4] of a-TiCuH$_x$, the magnetization recoveries during the T_1, T_{1D}, and T_2 measurements were always exponential indicating the a-TiCuH$_x$ samples were essentially single phase.

III. RESULTS

Figure 1 compares the room-temperature proton line shapes for crystalline TiCuH$_{0.94}$ and a-TiCuH$_{1.35}$. Whereas TiCuH$_{0.94}$ exhibits the nearly Gaussian line shape and short T_2^* expected[14] for immobile "rigid-lattice" protons, a motionally narrowed exponential free-induction decay (FID) is obtained for a-TiCuH$_{1.35}$. Cooling the a-TiCuH$_x$ samples below 220 K leads to the rigid-lattice line shape. A dipolar second moment (M_{2D}) of 14.8(5) G^2 was obtained at 90 K for a-TiCuH$_{1.4}$ and is slightly smaller than the value of 17.8(8) G^2 for TiCuH$_{0.94}$.[5] Since M_{2D} is determined[14] by the separation and coordination of the magnetic nuclei, these results imply the average proton-proton distances are somewhat larger in a-TiCuH$_x$. Although it is not possible to quantitatively deduce the local structure in amorphous solids from M_{2D} data alone, the similar M_{2D} values for TiCuH$_{0.94}$ and a-TiCuH$_x$ are consistent with the broad distribution of hydrogen in "average" tetrahedral interstitial sites as suggested by the inelastic neutron scattering spectra.[10]

(a) TiCuH$_{0.94}$ — Solid Echo at 300K



(b) a–TiCuH$_{1.35}$ — FID at 300K

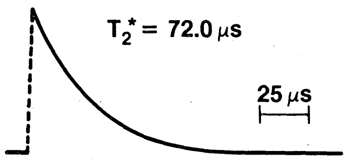


FIG. 1. Comparison of proton line shapes for crystalline TiCuH$_{0.94}$ (Ref. 5) and amorphous TiCuH$_{1.35}$ at 34.5 MHz where the dashed lines identify the signal decays masked by the rf pulses and probe ringdown voltages.

The temperature dependences of the proton relaxation times T_2^* and T_2' for TiCuH$_{0.94}$ and a-TiCuH$_{1.3}$ are compared in Fig. 2. Although motional narrowing begins near 230(10) K for a-TiCuH$_{1.3}$, TiCuH$_{0.94}$ requires temperatures near 440(10) K before the hydrogen diffusion rate is sufficient to give significant T_2^* and T_2' increases. The hydrogen diffusion E_a values, as deduced from the temperature dependence of the T_2' and T_{2m} data, are summarized in Fig. 3. The relaxation time behaviors for two a-TiCuH$_x$ compositions are seen to be nearly identical. Similar results were also obtained below 300 K for three oth-

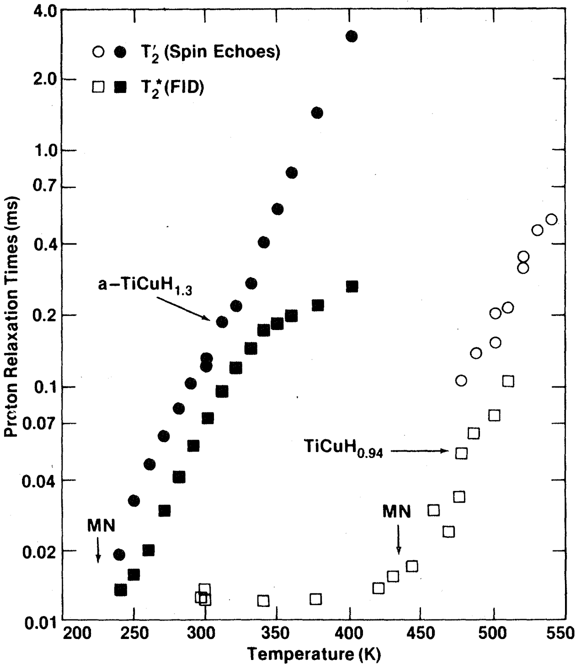


FIG. 2. Spin-spin relaxation times for crystalline TiCuH$_{0.94}$ and a-TiCuH$_{1.3}$ where MN denotes the observable onset of motional narrowing of proton line shapes.

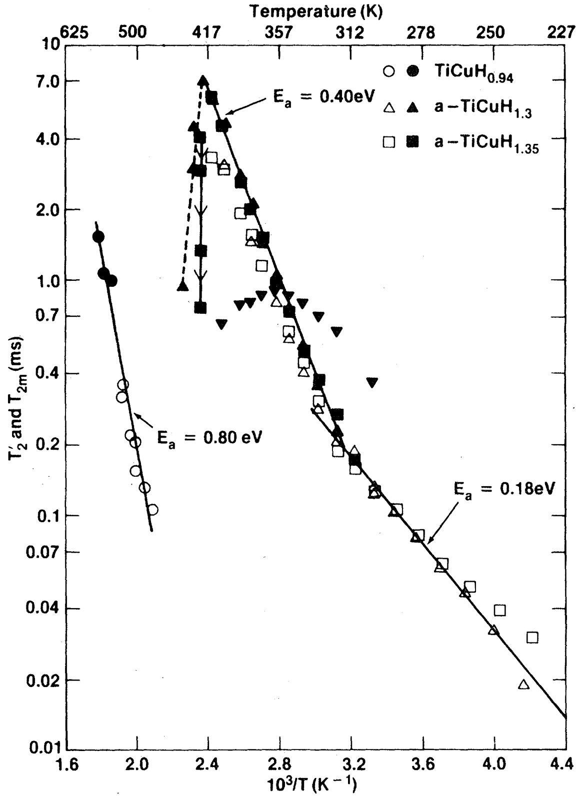


FIG. 3. Comparison of proton T_2' (open symbols) and T_{2m} (closed symbols) relaxation times for crystalline $TiCuH_{0.94}$ and two amorphous a-$TiCuH_x$ samples. Irreversible decreases in T_{2m} observed above 420 K correspond to partial decomposition of a-$TiCuH_x$ phase as described in text. The symbols ▼ denote T_{2m} values for sample a-$TiCuH_{1.35}$ after partial decomposition at 420 K which is indicated by the vertical line with arrows. The activation energies (E_a) for hydrogen diffusion are also included.

er a-$TiCuH_x$ samples. Hence, the present observations are regarded as completely representative of the amorphous a-$TiCuH_x$ phase. The T_2 relaxation times for a-$TiCuH_x$ indicate distinct non-Arrhenius behavior with two E_a values and a rather sharp break near 320 K. Only a single diffusion process with the much larger $E_a = 0.80$ eV is observed for crystalline $TiCuH_{0.94}$. Figures 2 and 3 also exhibit the relaxation

$$T_2^* < T_2' < T_{2m} \tag{1}$$

for each temperature where the three parameters have been simultaneously measured. This is a rather common feature for T_2 relaxation times in systems with moderate to large inhomogeneous magnetic contributions which includes most metal hydrides.[14] Because the spin-echo and CPMG techniques are increasingly effective in reducing the various inhomogeneous contributions[15] to spin-spin relaxation, the longest homogeneous relaxation mechanism (i.e., modulation of dipolar couplings via diffusion[13–15]) becomes the limiting T_2 parameter for the CPMG sequence. Unfortunately, the CPMG technique[15] can only be applied when $T_2 \gtrsim 0.2$ ms. However, the spin-echo sequence usually[14,15] gives reliable T_2 values in this region unless the inhomogeneous contributions are extremely large, which is not the case for the $TiCuH_x$ samples.

Figure 3 clearly illustrates an anomalous decrease in the proton T_2 relaxation times that occurs near 420 K for both a-$TiCuH_x$ samples. When the temperature is raised to 424 K, sequential CPMG measurements of a-$TiCuH_{1.35}$ gave T_{2m} values which irreversibly decreased by an order of magnitude over a period of only 50 min. The subsequent T_{2m} values obtained upon cooling this sample are seen in Fig. 3 to be entirely different from the results measured during the initial heating to 420 K. Furthermore, after the a-$TiCuH_x$ samples were heated to 420–430 K the formerly exponential T_1 recoveries becomes distinctly nonexponential and the proton line shapes consist of both fast (i.e., $T_2^* \approx 10$ μs) and the previous slowly decaying components. These irreversible changes in the proton NMR parameters directly correspond to the lower of two exothermic peaks observed at about 433 and 510 K during differential thermal analysis (DTA) measurements[3,4] on similar a-$TiCuH_x$ samples. These DTA peaks are associated[3,4] with the decomposition of the initially homogeneous a-$TiCuH_x$ phase into a mixed phase to ultimately produce crystalline TiH_x and Cu metal. The presence of both crystalline TiH_x and Cu metal after heating a-$TiCuH_x$ above 407 K has been verified by x-ray diffraction patterns.[4] This transformation is apparently incomplete under the present experimental conditions (i.e., about 1 to 2 h between 420 and 430 K) since the NMR relaxation times imply relatively immobile protons corresponding to the γ-TiH_x phase[7,9] as well as the more mobile protons in a partially depleted a-$TiCuH_x$ phase. A somewhat similar decomposition of crystalline $TiCuH_{0.94}$ to produce a mixture of TiH_x-Cu was detected in the previous NMR study.[5] However, disproportionation in $TiCuH_{0.94}$ did not occur until about 560 K when this sample was measured under similar conditions.

The dipolar relaxation time T_{1D} (Ref. 12) permits the study of diffusion behavior at temperatures below the motional narrowing region. Figure 4 summarizes the T_{1D} as well as T_1 data for crystalline $TiCuH_{0.94}$ and two a-$TiCuH_x$ samples. The T_{1D} data for $TiCuH_{0.94}$ yield an E_a value essentially equal to the T_2 results in Fig. 3 and suggest that a unique diffusion process is responsible in the combined temperature range. Although the T_{1D} results for a-$TiCuH_x$ are entirely consistent with motional narrowing beginning near 230 K, the T_{1D} data lead to even smaller E_a values below 220 K. Both a-$TiCuH_x$ sam-

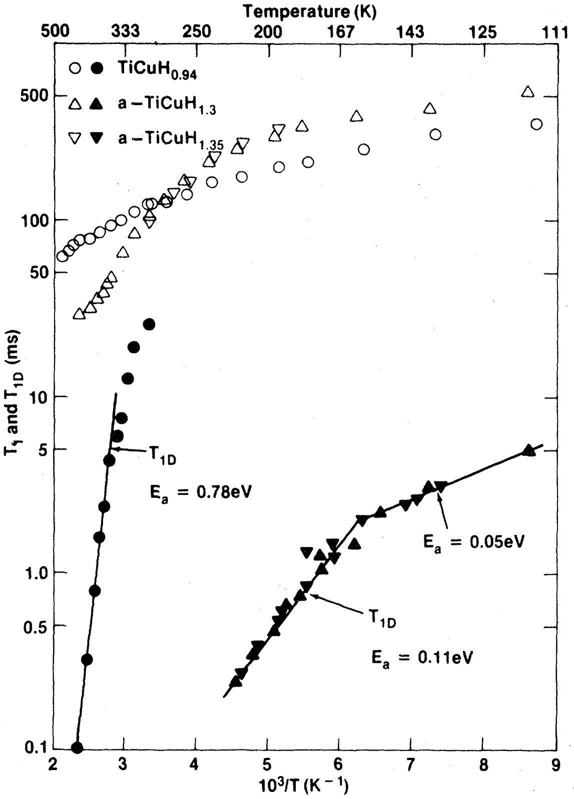


FIG. 4. Proton spin-lattice–lattice relaxation times T_1 (open symbols) and dipolar relaxation times T_{1D} (closed symbols) measured at 34.5 MHz.

ples again show similar behavior.

The T_1 values in Fig. 4 decrease more rapidly with temperature for a-TiCuH$_x$ samples than for TiCuH$_{0.94}$ reflecting the greater hydrogen diffusion rate in a-TiCuH$_x$. However, the previously described TiH$_x$-Cu decompositions have prevented determination of the expected[14] T_1 minima and seriously limits any meaningful analysis[7] of diffusion parameters from the available T_1 data. Consequently, the T_1 results have not been explicitly utilized to characterize diffusion behavior in a-TiCuH$_x$ and will not be discussed any further.

IV. DISCUSSION

The NMR techniques have been very successful in evaluating diffusion behavior in many metal-hydrogen systems.[14] In the specific case of protons, which do not possess a nuclear quadrupole moment, atomic motion induces a time dependence to the dipolar interactions to become the dominant nuclear relaxation mechanism[14] when hydrogen diffusion coefficients are between 10^{-12} and 10^{-5} cm^2/s. The proton relaxation times are formally expressed[14] via the diffusion correlation time τ_c which is related to D through

$$D = Ka^2/\tau_c \ , \qquad (2)$$

where K is a numerical parameter accounting for symmetry and possible correlation effects and a is the mean jump distance. Although the nuclear relaxation times provide indirect diffusion measurements, there have been several quantitative comparisons[14,16] between directly measured diffusion coefficients and D values calculated with τ_c from proton relaxation times in metal hydrides. At temperatures above motional narrowing of the proton line shape [i.e., when $\tau_c^{-1} > (\gamma_H^2 M_{2D})^{1/2}$ where γ_H is the proton gyromagnetic ratio and M_{2D} is the rigid-lattice dipolar second moment] τ_c can be determined from the experimental T_2 data through the relation

$$\tau_c^{-1} = \gamma_H^2 M_{2D} T_2 \ . \qquad (3)$$

This expression along with the M_{2D} measured at 90 K for a-TiCuH$_{1.4}$ and the average T_2' value in Fig. 3 for the a-TiCuH$_x$ samples have been used to calculate τ_c^{-1} at 300 K. Table I compares the E_a and τ_c^{-1} (300 K) values for a-TiCuH$_x$ with the results for

TABLE I. Comparison of hydrogen diffusion parameters in crystalline and glassy TiCuH$_x$ and γ-phase TiH$_x$ as deduced from proton relaxation times.

Hydride	E_a (eV)	Temperature range (K)	τ_c^{-1} (300 K) (s^{-1})	Reference
a-TiCuH$_{1.3-1.35}$	0.40(2)	320–420	· · ·	Present work
a-TiCuH$_{1.3-1.35}$	0.18(2)	250–320	1.4×10^6	Present work
a-TiCuH$_{1.3-1.35}$	0.11(2)	160–220	· · ·	Present work
a-TiCuH$_{1.3-1.35}$	0.05(1)	115–160	· · ·	Present work
TiCuH$_{0.94}$	0.79(3)	350–570	13	Bowman *et al.* (Ref. 5)
TiH$_{1.81}$	0.51(1)	280–625	3.9×10^3	Korn and Goren (Ref. 9)
TiH$_{1.90}$	0.51(1)	280–625	2.4×10^3	Korn and Goren (Ref. 9)

crystalline $TiCuH_{0.94}$ (Ref. 5) and γ-TiH_x.[9] Although it is possible (in principle) to uniquely identify the diffusion jump distance a in the crystalline hydrides,[5,16] the extensive variations in the local symmetries about the nominally tetrahedral hydrogen interstitial sites in a-$TiCuH_x$ (Ref. 10) prevents the assignment of a unique a value for the glassy phase. However, the nearly-equal rigid-lattice M_{2D} for $TiCuH_{0.94}$ and a-$TiCuH_{1.4}$ strongly suggest that the "average" hydrogen—hydrogen separations, which should directly correspond to a, are very similar in the crystalline and glassy phase. Hence, the τ_c^{-1} parameters should provide reasonable estimates of the relative hydrogen diffusion rates in a-$TiCuH_x$ as well as in the crystalline hydride phases.

A primary point to be made from the τ_c^{-1} (300 K) values in Table I is that the apparent hydrogen diffusion rate in glassy a-$TiCuH_{1.3}$ is several hundred times larger relative to γ-TiH_x and 10^5 larger than the value for crystalline $TiCuH_{0.94}$. These observations contradict the recent suggestion[1] that interstitial diffusion in amorphous alloys should be smaller than in the crystalline phase because the diffusing atoms can be trapped at larger interstitial sites in the amorphous alloy. However, Birac and Lesueur[17] have measured the diffusion coefficient of interstitial lithium to be at least 10^2 times faster in the amorphous $Pd_{80}Si_{20}$ alloy than in the same crystalline alloy. Hence, the available experimental evidence indicates a very significant enhancement of interstitial diffusion occurs in the amorphous phases of two completely unrelated alloy systems. Additional comparative studies of the interstitial diffusion behavior of amorphous and crystalline phases in other alloys are needed to establish whether this may be a general phenomena.

Table I also shows that hydrogen diffusion in crystalline $TiCuH_{0.94}$ and γ-TiH_x exhibit Arrhenius behavior over wide temperature ranges. A single diffusion mechanism involving hydrogen jumps to specific vacant interstitial sites is believed responsible[7,9,16] while the different E_a values reflect the structure-sensitive jump paths as described previously.[5] However, a more complex temperature dependence in apparent hydrogen mobility is obtained for glassy a-$TiCuH_{1.3}$ where four regions with different E_a values have been identified between 115 and 420 K.

There are several contributing factors to the hydrogen diffusion processes in a-$TiCuH_{1.3}$. Although the H atoms in a-$TiCuH_{1.3}$ appear[10] to retain the predominantly tetrahedral metal coordination of crystalline TiCuH and γ-TiH_2, the hydrogens can have different ratios of titanium and copper atoms as nearest neighbors (however, Cu_4 and $TiCu_3$ coordination are not expected since copper does not form a stable hydride) as well as possible interstitial sites with nominal octahedral symmetry.[10] The depths of the potential wells for the hydrogen probably decrease as the number of neighboring copper atoms increases. Furthermore, the glassy structure in a-$TiCuH_x$ should increase the probability for vacant interstitial sites occurring next to occupied hydrogen sites. Diffusion at low temperatures should be mainly determined by a few hydrogen atoms in the most shallow potential-wells and nuclear-spin cross-relaxation processes[18] can communicate these low E_a contributions to the entire proton spin system. As the temperature is raised, various higher-energy diffusion processes contribute until the average mobility of all the protons become sufficient to first produce motional narrowing and the subsequent T_2 increase and T_1 decrease seen in Figs. 2–4. If the diffusion mechanism in a-$TiCuH_x$ involved a large number of jump paths each with a different activation energy, the non-Arrhenius temperature dependence should exhibit a nearly continuous change with temperature. However, the proton relaxation times T_{1D} and T_2 for a-$TiCuH_{1.3}$ in Figs. 3 and 4 give distinct and rather sharp breaks at specific temperatures. This behavior implies that only a relatively few (tentatively, four) alternative jump paths may contribute to hydrogen diffusion in a-$TiCuH_x$. These allowed paths may be dictated by short-range order in the local structure of the glass. Unfortunately, there is currently no conclusive information on the type and distribution of local symmetries about the hydrogen interstitials and a detailed interpretation of diffusion in a-$TiCuH_x$ must be deferred. However, it may be significant that the largest E_a for a-$TiCuH_x$ (i.e., 0.4 eV) is only half the value for the direct tetrahedral-tetrahedral jump in crystalline $TiCuH_{0.94}$ (Ref. 5) and is also smaller than E_a for γ-TiH_x.[7,9] Hence, the probable diffusion paths in a-$TiCuH_x$ do not directly correspond to those in the crystalline phases. Because several processes can simultaneously occur in a-$TiCuH_x$, great caution should be exercised before assigning E_a values to specific jump paths in the glassy phase since the experimental activation energies actually reflect temperature-dependent averages of the alternative paths.

As a final comment, the ternary $TiCuH_x$ phase has been shown[3] to be thermodynamically less stable than the mixture of TiH_x-Cu phases. In fact, the presumably very-low-metal-atom diffusion rates in TiCu below about 250 °C are probably responsible for the formation of the metastable ternary hydride phase. The irreversible decomposition of a-$TiCuH_{1.3}$ at about 425 K occurs well below the similar decomposition at 560 K in crystalline $TiCuH_{0.94}$. This difference is entirely consistent with the enhanced diffusion rate in the amorphous phase promoting a kinetics restricted phase transformation into the stable TiH_x-Cu mixed phases at significantly lower temperatures relative to the analogous transformation in the crystalline phase.

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