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HYDROGEN DIFFUSION AND ELECTRONIC STRUCTURE

IN CRYSTALLINE AND AMORPHOUS TiCuH_y

R. C. Bowman, Jr.*
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

A. J. Maeland
Materials Research Center
Allied Chemical Corporation
Morristown, New Jersey 07960

W.-K. Rhim
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91103

J. Y. Lynch**
Brookhaven National Laboratory
Upton, New York 11973

ABSTRACT

Hydrogen diffusion behavior and electronic properties of crystalline TiCuH_0.9, Ti_2CuH_1.9, and Ti_2CuH_2.63, and amorphous a-TiCuH_1.4 are studied using proton relaxation times, proton Knight shifts, and magnetic susceptibilities. Crystal structure and hydrogen site occupancy have major roles in hydrogen mobility. The density of electron states at E_F is reduced in amorphous a-TiCuH_1.4 compared to the crystalline hydrides.

The crystalline intermetallics TiCu and Ti_2Cu and the amorphous Ti_1-yCu_y (0.3 ≤ y ≤ 0.7) alloys directly react with gaseous hydrogen to form crystalline and amorphous ternary hydrides, respectively, providing the temperature is maintained below 200°C. A recent nuclear magnetic resonance (NMR) study of the proton relaxation times indicated a much higher hydrogen mobility in amorphous a-TiCuH_1.4 compared to crystalline hydrides.

*On leave from current address: Monsanto Research Corporation, Mound, Miamisburg, Ohio 45342.
**Current address is Materials Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960.
to polycrystalline TiCuH$_{0.94}$. The increased disorder$^2$ of interstitial hydrogen occupancy in a-TiCuH$_x$ has been suggested$^3$ for the enhanced mobility in the amorphous phase. The present paper describes further NMR studies of diffusion in crystalline and amorphous TiCuH$_x$ as well as crystalline Ti$_2$CuH$_x$. Furthermore, the electronic structure has been investigated using magnetic susceptibility, proton spin-lattice relaxation time ($T_1$), and proton Knight shift ($G_H$) measurements.

Table 1 summarizes the structural properties of the TiCuH and Ti$_2$CuH$_x$ samples as deduced from x-ray diffraction, neutron scattering, and proton lineshape parameters. The preparation procedures have been previously described.1,5

Table 1. Descriptions of TiCuH and Ti$_2$CuH and Hydrogen Diffusion Activation Energies ($E_a$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal Sublattice Structure</th>
<th>Probable Hydrogen Site Occupancies</th>
<th>$E_a$ (eV)</th>
<th>Temperature Range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCuH$_{0.94}$</td>
<td>Tetragonal</td>
<td>94% Ti$_4$ only</td>
<td>0.84±0.02</td>
<td>465 - 560</td>
</tr>
<tr>
<td>a-TiCuH$_{1.4}$</td>
<td>Amorphous</td>
<td>Mixed (mostly Ti$_4$ with some Ti$_4$-$\gamma$Cu$_y$ and octahedral)</td>
<td>0.45±0.02</td>
<td>357 - 410</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.185±0.01</td>
<td>208 - 357</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.09±0.01</td>
<td>150 - 207</td>
</tr>
<tr>
<td>Ti$<em>2$CuH$</em>{1.9}$</td>
<td>Orthorhombic (?)</td>
<td>95% Ti$_4$ (some Ti$_2$Cu$_4$ likely)</td>
<td>0.35±0.02</td>
<td>290 - 519</td>
</tr>
<tr>
<td>Ti$<em>2$CuH$</em>{2.63}$</td>
<td>Orthorhombic (?)</td>
<td>100% Ti$_4$ and 63% Ti$_2$Cu$_4$</td>
<td>0.29±0.02</td>
<td>290 - 395</td>
</tr>
</tbody>
</table>

Hydrogen diffusion behavior has been evaluated using the temperature dependence of the proton rotating-frame spin-lattice relaxation times$^6$ ($T_{1\rho}$) where the spin-locking field was about 7.3G and the proton resonance frequency was 34.5 MHz. The temperature dependences of the $T_{1\rho}$ data for Ti$_x$CuH$_y$ are shown in Fig. 1. Table 1 summarizes the diffusion activation energies ($E_a$) that have been deduced from the $T_{1\rho}$ data. Although a single $E_a$ corresponding to Arrhenius behavior represents proton mobility in the crystalline TiCuH$_{0.94}$ and Ti$_2$CuH$_x$, three $E_a$ values are required for amorphous a-TiCuH$_{1.4}$, which confirms the behavior previously seen$^5$ in a-TiCuH$_{1.3}$. Furthermore, $E_a$ is greatly reduced when protons occupy sites in addition to the tetrahedral Ti$_4$ interstitials. This effect is seen in both crystalline Ti$_2$CuH$_x$ and amorphous a-TiCuH$_{1.4}$. From a consideration of the TiCu and Ti$_2$Cu crystal structures,$^{1,4}$ hydrogen diffusion in crystalline TiCuH can only occur by nearest neighbor jumps between the Ti$_4$ sites,
while jumps through the intermediate Ti$_2$Cu$_x$ sites become possible in Ti$_2$CuH$_x$. This probably accounts for the lower $E$ values for Ti$_2$CuH$_x$ and similar (or even easier) jump-paths are available in the more disordered amorphous phase.

The magnetic susceptibilities ($\chi_m$) for Ti$_y$Cu$_x$ were measured between 80 K and 300 K and are summarized in Fig. 2. Although the $\chi_m$ values in Fig. 2 have been extrapolated to infinite magnetic field, the field-dependent ferromagnetic contribution was negligible except for a-TiCuH$_{1.4}$, which appears to have some magnetic impurities as well as an opposite temperature dependence for $\chi_m$. There are several contributions to $\chi_m$, but only the paramagnetic term $\chi_p$ is directly related to $N(E_F)$, the density of electron states at the Fermi level $E_F$. Hence, caution should be exercised in correlating $\chi_m$ differences only to $N(E_F)$ changes. In particular, the larger $\chi_m$ for a-TiCuH$_{1.4}$ compared to TiCuH$_{0.8}$, probably reflects either ferromagnetic or orbital contributions and not a greater $N(E_F)$ for the amorphous phase. However, the unusual $\chi_m$ increase with hydrogen content for Ti$_2$CuH$_x$ is believed to actually correspond to $N(E_F)$ becoming larger since the proton $T_1$ and $Q_K$ parameters also indicate $N(E_F)$ increasing from Ti$_2$CuH$_{1.9}$ to Ti$_2$CuH$_{2.63}$.

![Fig. 2. Magnetic susceptibility values for TiCuH$_x$ and Ti$_2$CuH$_x$.](image)
The proton $T_1$ and $\sigma_K$ were measured at 56.4 MHz using methods previously described. The $\sigma_K$ values are referenced to tetramethylsilane. Table 2 summarizes the $\sigma_K$ and $(T_1 T)^{-1/2}$ parameters, which are directly proportional to $N(E_F)$, at the upper and lower temperature limits of the present NMR measurements. The negative $\sigma_K$ values in Table 2 indicate that core-polarization with d-electrons dominates proton hyperfine interactions in Ti$_y$Cu$_x$H$_x$ where the population of d-states is much larger than s-states as has been previously found in other Ti-based hydrides. Furthermore, the proton parameters suggest $N(E_F)$ is significantly reduced in a-TiCuH$_{1.4}$ compared to crystalline TiCuH$_{0.94}$, while $N(E_F)$ increases with content in crystalline Ti$_2$CuH$_{1.9}$. However, a more detailed analysis based upon generalized Korringa relations shows increased s-electron contact hyperfine interactions in the Ti$_2$CuH$_{2.63}$ samples.

More extensive discussions of hydrogen diffusion and the electronic structures of Ti$_y$Cu$_x$H$_x$ will be published elsewhere.

Table 2. Proton Parameters $(T_1 T)^{-1/2}$ and Knight Shifts $\sigma_K$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$ (K)</th>
<th>$(T_1 T)^{-1/2}$</th>
<th>$\sigma_K$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCuH$_{0.94}$</td>
<td>300</td>
<td>0.163</td>
<td>-120</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.150</td>
<td>-107</td>
</tr>
<tr>
<td>a-TiCuH$_{1.4}$</td>
<td>210</td>
<td>0.113</td>
<td>- 77</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.108</td>
<td>- 87</td>
</tr>
<tr>
<td>Ti$<em>2$CuH$</em>{1.9}$</td>
<td>300</td>
<td>0.118</td>
<td>- 67</td>
</tr>
<tr>
<td></td>
<td>115</td>
<td>0.115</td>
<td>- 69</td>
</tr>
<tr>
<td>Ti$<em>2$CuH$</em>{2.63}$</td>
<td>300</td>
<td>0.140</td>
<td>- 85</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.145</td>
<td>- 91</td>
</tr>
</tbody>
</table>

ACKNOWLEDGEMENTS

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REFERENCES

Fig. 1. Proton T₁₂ relaxation times with $H_1 = 7.3$ G at $v_H = 34.5$ MHz.