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PROTON NMR STUDIES OF THE ELECTRONIC .

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STRUCTURE OF ZrH

Attalla*, R. C. Bowman, Jr.*, B. D. Craft*, E. L. Vanturini**, and W.-K. Rhim***

- *Monsanto Research Corporation-Mound Miamisburg, Ohio 45342
- **Sandia National Laboratories Albuquerque, New Mexico 87185
- ***Jet Propulsion Laboratory California Institute of Technology Pasadena, California 91103

ABSTRACT

The proton spin-lattice relaxation times and Knight shifts have been measured in f.c.c. (δ -phase) and f.c.t. (ϵ -phase) ZrH_x for 1.5 $\leq x \leq 2.0$. Both parameters indicate that $N(E_F)$ is very dependent upon hydrogen content with a maximum occurring at $2rH_{1.83}$. This behavior is ascribed to modifications in $N(E_F)$ through a fcc-fct distortion in ZrH_{acc} accounted with a Jahn-Teller effect.

The electronic properties of the non-stoichiometric dihydrides of the IVB metals Ti, Zr, and Hf have been the subjects of numerous theoretical¹⁻³ and experimental⁴⁻¹⁰ studies. Much of this interest has focused on the temperature and composition dependent fcc to fct phase transition that has been associated^{1/2/4} with a Jahn-Teller type mechanism, as well as the more general problem of the character of the metal-hydrogen bonds.^{1/5-8} Although there have been several recent nuclear magnetic resonance (NMR) studies related to the electronic structure of TiH, ⁶⁻⁸ only limited NMR results^{9/10} address the electronic properties of δ -phase (fcc) and ε -phase (fct) ZrH. In the present work, the temperature and composition dependences of the proton spin-lattice relaxation times (T₁) and Knight shifts (σ) have been measured in high-purity polycrystalline ZrH for 1.5 $\leq x \leq 2.0$. These parameters, which are related¹¹ to the densities of electron

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states $N(E_{p})$ at the Fermi energy E_{p} , show the dominance of the corepolarization hyperfine interaction with the Zr d-electrons and yield a maximum in $N(E_{p})$ near x = 1.83. These observations support the Jahn-Teller mechanism^{1,4} for the tetragonal distortion and are consistent with recent APW band-theory calculations³ of fcc ZrH₂ and photoemission spectra⁵ for ZrH₂.

The ZrH_x samples were prepared by direct reactions between purified H₂ gas and zone-refined Zr foils (Materials Research Corporation - MARZ grade). The ZrH_x foils were ground under an argon atmosphere to produce powders that were sealed in evacuated glass tubes. The T₁ values were obtained by the standard inversion-recovery method at the proton frequency of 34.5 MHz. The previously described⁸ zero-crossing method produced the $\sigma_{\rm K}$ values, which are relative to an external reference of tetramethylsilane, for a resonance frequency of 56.4 MHz. The $\sigma_{\rm K}$ values have a precision of ±2 ppm while the exponential T₁ recoveries yielded T₁ with a precision of ±3%. The T₁ values were estained between 170 K and 310 K, as shown in Figs. 1 and 2, respectively. There was no unusual temperature behavior for either parameter. Below 310 K, the proton T₁ values are assumed to be dominated by the conduction electron component T₁ as found previously.

The composition and temperature behavior of the proton $\sigma_{\rm K}$ and $({\bf T_{10}} \ {\bf T})^{-\frac{1}{2}}$ parameters for ZrH_x are summarized in Fig. 3 where T is the absolute temperature. The major feature for $({\bf T_{10}} \ {\bf T})^{-\frac{1}{2}}$ is an increase above x = 1.65 to reach a maximum near x = 1.83 before decreasing smoothly up to x = 2.00. $({\bf T_{10}} \ {\bf T})^{-\frac{1}{2}}$ exhibits the largest temperature dependence for 1.80 \leq x \leq 1.85 (i.e., at the peak). Similar behavior is noted for the proton $\sigma_{\rm K}$ parameters; however, neither the composition nor temperature dependence of $\sigma_{\rm K}$ is as large as seen for $({\bf T_{10}} \ {\bf T})^{-\frac{1}{2}}$.

The proton T_{10} and σ_{K} parameters are related to the electronic structure of a metal hydride through the hyperfine fields¹¹ produced at the proton sites. Since the d-electron orbital terms¹¹ appear to make insignificant contributions to the proton parameters in several metal hydrides,^{7,8} the σ_{K} and T_{10} parameters can be separated as

$$\sigma_{\kappa} = 2\mu_{B}[H_{hf}(s)N_{s}(E_{F}) + H_{hf}(d)N_{d}(E_{F})]$$
(1)

$$\frac{1}{T_{le}^{T}} = 4\pi \gamma_{H}^{2} k_{B}^{\{[H_{hf}(s)N_{s}(E_{F})]^{2} + [H_{hf}(d)N_{d}(E_{F})]^{2}q\}}.$$
 (2)

Here, H_{n_1} (s) and H_{n_1} (d) are the hyperfine fields for the Fermi contact interaction with unpaired s-electrons and transferred "core" polarization from the s-d exchange with metal d-states, respectively; μ_{g} is the Bohr magnetron, γ_{H} is the proton gyromagnetic moment; k_{g} is the Boltzmann's constant; and the reduction factor $q = 1/3[f(t_{2g})]^2$ $+ 1/2[1-f(t_{2g})]^2$ in a cubic structure where $f(t_{2g})$ is the fractional



Fig. 1. Proton T₁ for ZrH_x at $v_H = 34.5$ MHz.

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Fig. 2. Proton Knight shifts for 7rH, measured by multiple-pulse zero-cross technique at 56.4 MHz.



Fig. 3. Composition dependence of proton $(T_{1_0}T)^{-\frac{1}{2}}$ and σ_{1_0} for ZrH₁.

character of the t_{2g} d-orbitals at E_F . The H_{hf} (s) is always positive, but H_{hf} (d) is usually negative.¹¹ Thus, although the contact and core polarization terms are additive for $(T_{1e}T)^{-\frac{1}{2}}$, a large cancellation can occur in σ_{κ} .

The negative proton $\sigma_{\rm K}$ values in Fig. 2 clearly indicate that the core-polarization term exceeds the contact term in δ -ZrH_x and ϵ -ZrH_x, which implies N_d(E_r)>>N_s(E_r) in these hydrides. Similar conclusions have been made for several other hydrides including γ -TiH_x,⁷ Ti_{1-y}V_yH_x,⁸ TiCuH_x,¹² and TiCr₂H_x;¹³ hence, a relatively large N_d(E_r) seems to be a general property of the hydride phases formed by group IVB metals and of at least some alloys containing Ti. A more detailed analysis of the proton $\sigma_{\rm K}$ and (T_{1e} T)^{-1/2} values for ZrH_x suggests substantial s-electron contact (or, perhaps, some orbital) contribution in δ -phase ZrH_{1.60} while the core-polarization seems to be the exclusive hyperfine interaction in ϵ -phase ZrH_x. The composition dependence of $(T_{1e}T)^{-\frac{1}{2}}$ and σ_{K} in Fig. 3 is consistent with the available band theory calculations for TiH₂,^{1/2} and Z_zH₂,³ as well as the Jahn-Teller mechanism^{2/4} for the fcc-fct transition. Briefly, N_d (E_F) is apparently constant in fcc δ -ZrH_x (x < 1.65) as the E_F level moves upward with x, but adding more hydrogen above 1.65 causes E_F to enter the band region where N_d (E_F) increases rapidly until x \sim 1.83. However, because of the electronic instability of a large N_d (E_F) the tetragonal distortion continually increases, which will tend to reduce the N_d (E_F) value as x becomes larger. The competition between N_d (E_F) increasing with more hydrogen and decreasing with the Jahn-Teller tetragonal distortion produces the (T_{1e}T)^{-1/2} maximum near x = 1.83. This general behavior corresponds to changes seen in the photoemission spectra⁵ of ZrH_x as hydrogen content varies. A more detailed discussion of the electronic structure and proton parameters will be published elsewhere.

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