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PROTON NMR STUDIES OF THE ELECTRONIC
STRUCTURE OF ZrH_x

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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 $1.5 < x < 2.0$. Both parameters indicate that $N(E_F)$ is very dependent upon hydrogen content with a maximum occurring at $ZrH_{1.83}$. This behavior is ascribed to modifications in $N(E_F)$ through a fcc-fct distortion in ZrH_x associated 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_x ,⁶⁻⁸ only limited NMR results^{9,10} address the electronic properties of δ -phase (fcc) and ϵ -phase (fct) ZrH_x . In the present work, the temperature and composition dependences of the proton spin-lattice relaxation times (T_1) and Knight shifts (σ_K) have been measured in high-purity polycrystalline ZrH_x for $1.5 < x < 2.0$. These parameters, which are related¹¹ to the densities of electron

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states $N(E_F)$ at the Fermi energy E_F , show the dominance of the core-polarization hyperfine interaction with the Zr d-electrons and yield a maximum in $N(E_F)$ 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 ZrH_2 and photoemission spectra⁵ for ZrH_x .

The ZrH_x samples were prepared by direct reactions between purified H_2 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 T_1 values were obtained by the standard inversion-recovery method at the proton frequency of 34.5 MHz. The previously described⁶ zero-crossing method produced the σ_K values, which are relative to an external reference of tetramethylsilane, for a resonance frequency of 56.4 MHz. The σ_K values have a precision of ± 2 ppm while the exponential T_1 recoveries yielded T_1 with a precision of $\pm 3\%$. The T_1 values were measured over the temperature range 100 K to 300 K and the σ_K values were obtained 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 T_1 values are assumed to be dominated by the conduction electron component T_{1e} as found previously.^{9,10}

The composition and temperature behavior of the proton σ_K and $(T_1 \cdot T)^{-1/2}$ parameters for ZrH_x are summarized in Fig. 3 where T is the absolute temperature. The major feature for $(T_1 \cdot T)^{-1/2}$ is an increase above $x = 1.65$ to reach a maximum near $x = 1.83$ before decreasing smoothly up to $x = 2.00$. $(T_1 \cdot T)^{-1/2}$ 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 σ_K parameters; however, neither the composition nor temperature dependence of σ_K is as large as seen for $(T_1 \cdot T)^{-1/2}$.

The proton T_{1e} 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_{1e} parameters can be separated as

$$\sigma_K = 2\mu_B [H_{hf}(s)N_s(E_F) + H_{hf}(d)N_d(E_F)] \quad (1)$$

$$\frac{1}{T_{1e}T} = 4\pi \gamma_H^2 k_B \{ [H_{hf}(s)N_s(E_F)]^2 + [H_{hf}(d)N_d(E_F)]^2 q \}. \quad (2)$$

Here, $H_{hf}(s)$ and $H_{hf}(d)$ 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_B is the Bohr magneton, γ_H is the proton gyromagnetic moment; k_B 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

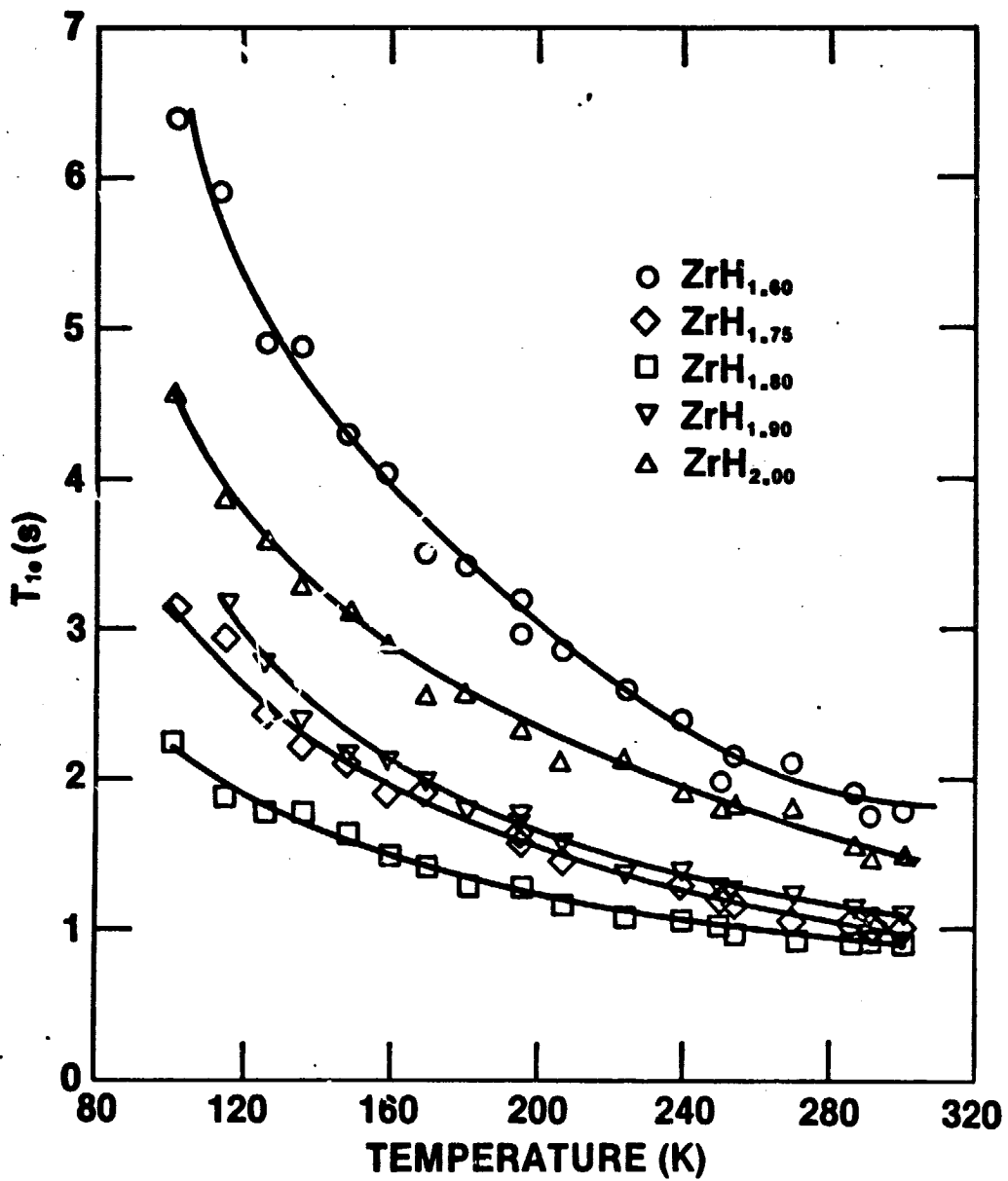


Fig. 1. Proton T_1 for ZrH_x at $\nu_H = 34.5$ MHz.

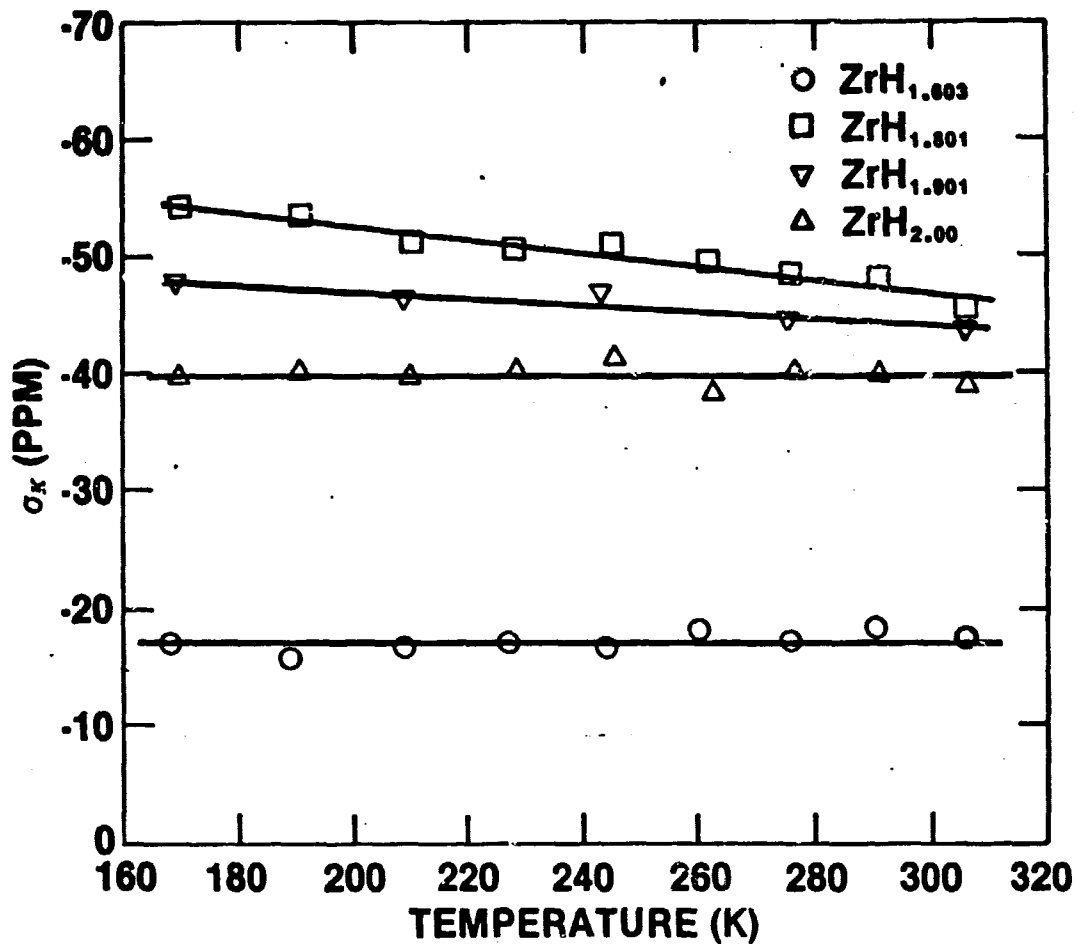


Fig. 2. Proton Knight shifts for ZrH_x measured by multiple-pulse zero-cross technique at 56.4 MHz.

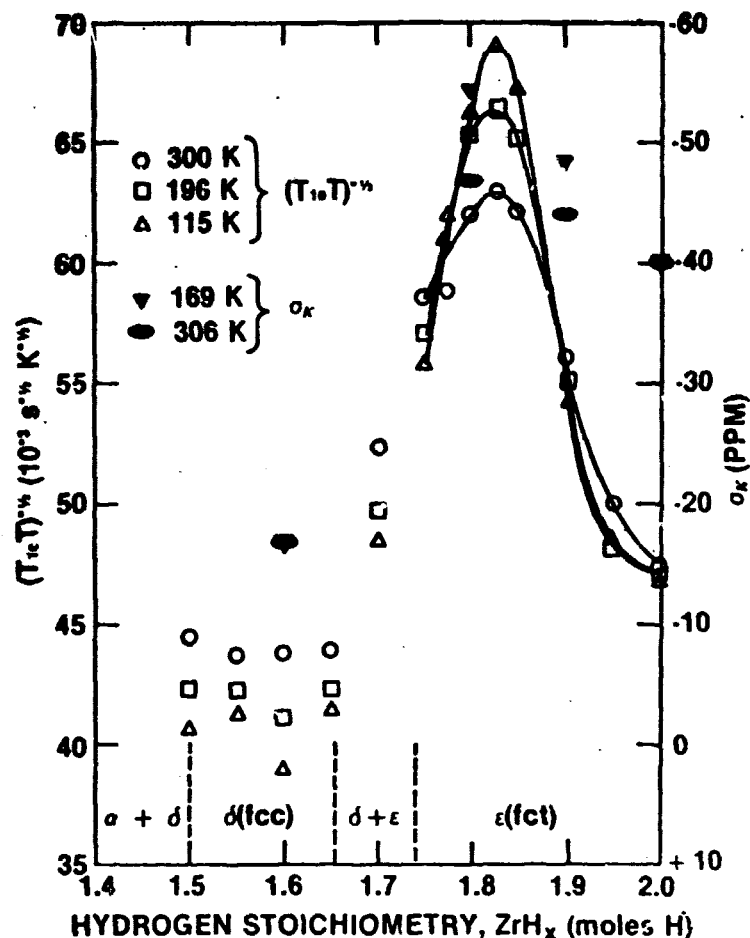


Fig. 3. Composition dependence of proton $(T_{1\rho}T)^{-1/2}$ and σ_K for ZrH_x .

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 $(T_{1\rho}T)^{-1/2}$, a large cancellation can occur in σ_K .

The negative proton σ_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 $N_d(E_f) \gg N_s(E_f)$ 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 $TiCr_2H_x$;¹³ hence, a relatively large $N_d(E_f)$ 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 σ_K and $(T_{1\rho}T)^{-1/2}$ 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 $(T_1, T)^{-1/2}$ and σ_K in Fig. 3 is consistent with the available band theory calculations for TiH_2 ,^{1,2} and ZrH_2 ,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 $x \approx 1.83$. 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 $(T_1, T)^{-1/2}$ 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.

ACKNOWLEDGEMENTS

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