that band[22]; the resulting hybridization should give rise to a substantial increase in band effective mass and a decrease in P_F with attendant changes in K and T_1.

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Nuclear-Magnetic-Resonance Investigation of Proton Motion in Scandium Hydride†

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Hydrogen diffusion processes in nonstoichiometric scandium hydrides have been investigated using transient nuclear-magnetic-resonance methods. Activation energies (E_A) were found to be strongly concentration dependent with two processes becoming evident as the hydrogen-to-metal ratio (x) approached 2. The variation of E_A with x is interpreted as an effect of non-rigid-band behavior for the electron states. Both relaxation-time analysis and rigid-lattice linewidths suggest appreciable occupation of octahedral sites normally vacant in other dihydrides.

I. INTRODUCTION

Scandium metal will dissolve hydrogen to form nonstoichiometric hydrides[1] with a maximum hydrogen-to-metal ratio (x) of 2. The scandium-hydrogen system differs from other group-III*B* metal systems in that no trihydride exists. This distinction undoubtedly reflects differences for the interatomic potentials which control the hydrogen diffusion processes. Nuclear-magnetic-resonance (NMR) methods are well suited for investigating these phenomena.

Previous studies of the III*B* metal hydrides (Sc, Y, and La) consist of measurements of the Knight shift and spin-lattice relaxation time (T_1) for both metal and proton.[2–5] Data from the metal resonance suggest similar electronic structure for these systems. A "protonic" model in which the hydrogen donates part of its electronic charge to the metal band was generally successful for analysis. However, such an analysis is not unique. In fact, recent band calculations,[6] also consistent with experimental work, indicate not only that a rigid-band concept is invalid, but that a relatively large amount of negative charge resides near the proton site.

We have carried out transient NMR measurements on the system ScH_x, $1.7 \geq x \leq 1.98$ in order to determine proton diffusion parameters. Section II describes our experimental procedure, Sec. III contains experimental measurements and data reduction, and Sec. IV presents a brief discussion of the data.

II. EXPERIMENTAL METHODS

Proton-spin-lattice relaxation-time measurements were accomplished using a conventional phase-coherent transient NMR spectrometer. A single platinum coil contained in a ceramic mold served as both transmitter and receiver with isolation effected by a tee-bridge cable arrangement. Experimental parameters of 20–30-G rotating field at 25 MHz were nominal. For signal averaging, a Biomation 102S high-speed digitizer was employed. In most cases, a spin echo following two equal-width pulses was monitored, but at the lower temperatures measurements were made on the free-induction decay produced by a single pulse. Temperatures to about 1000 K were generated in a feedback-controlled resistance heater with an overall accuracy of ±1 K. Resonance line shapes were recorded using a Varian 4210 spectrometer and these measurements were carried out at room temperature only.

Samples were prepared by exposing elemental scandium metal to hydrogen gas. The hydride powder was then mixed with NaCl for electrical insulation and sealed under vacuum in quartz vials.

III. RESULTS

A. Relaxation Rates

Spin-lattice relaxation-time data for all samples displayed minima characteristic of a diffusion-induced mechanism.[7] Figure 1 shows an example of these data. We have indicated on the figure the maximum contribution to T_1 from hyperfine interactions with conduction electrons. This value was determined from the maximum hyperfine-induced rate found[8] for TiH_x. An actual determination of the hyperfine contribution in the present case is prevented by the observation of a second diffusion process. In what follows, we simply neglect the electronic contribution and note that our conclusions are unaffected by this approximation. The temperature at which T_1 exhibits a minimum is 800 K for $\mathrm{ScH}_{1.98}$ and decreases to about 600 K for $\mathrm{ScH}_{1.7}$. At 1000 K the equilibrium vapor of hydrogen over ScH_x is near 1 Torr.[9] In our small sample vials, this pressure represents a negligible concentration change.

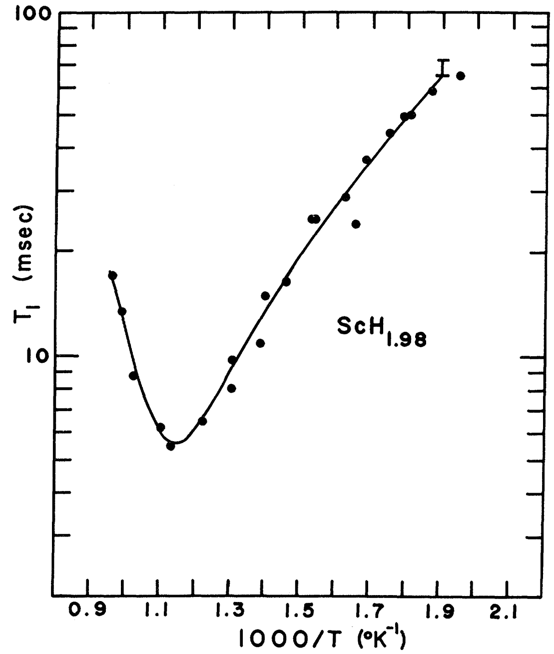

FIG. 1. Temperature dependence of proton spin-lattice relaxation time in $\mathrm{ScH}_{1.98}$. The error bar indicates an expected maximum contribution from conduction-electron interactions.

Nuclear spin-lattice relaxation times reflect the lifetime of a spin state. Atomic motion in the presence of the magnetic dipoles of other nuclei effectively presents a fluctuating field to the spin. These relaxation rates are enhanced when there is an appreciable field component at the Larmor frequency (ω_I). Such a situation clearly occurs as the atomic jump rate approaches ω_I, and it is in this range of jump rates that a minimum lifetime for the spin state is observed.

Since the magnetic moment of $^{45}\mathrm{Sc}$ is not negligible compared to that of the proton, the T_1 calculation must include both H—H and H—Sc interactions.[10] Exponential recovery is expected in the rapid-motion limit with

$$1/T_1 = \tfrac{3}{2}\gamma_I^2 C_I [J^{(1)}(\omega_I) + J^{(2)}(2\omega_I)] + \gamma_I^2 C_S [\tfrac{1}{12} J^{(0)}(\omega_I - \omega_S) + \tfrac{3}{2} J^{(1)}(\omega_I) + \tfrac{3}{4} J^{(2)}(\omega_I + \omega_S)] , \quad (1)$$

where I refers to proton, S refers to metal, $C_I = \gamma_I^2 \hbar^2 I(I+1)$, and $C_S = \gamma_S^2 \hbar^2 S(S+1)$. The spectral density functions $J^{(i)}(\omega)$ arise from spin correlations which reflect the probability for a spin component change of i units.[7] The other terms have their usual meanings. We shall assume an exponential correlation function and a single correlation time τ. This assumption yields

$$J^{(1)}(\omega) = \frac{4}{15} \frac{\tau}{1+\omega^2\tau^2} \sum_i r_i^{-6} , \quad (2)$$

where the sum extends over all occupied sites. Furthermore, for rapid motion or for high-symmetry lattices we have

$$J^{(2)}(\omega):J^{(1)}(\omega):J^{(0)}(\omega)=4:1:6\ . \qquad (3)$$

After combining (1)–(3), we can calculate τ given T_1.[11] Jump times for hydrogen are identified with τ and thus an Ahrenius plot can be constructed. Equation (1) yields a minimum T_1 of 12 msec at $\omega\tau = 0.645$ for ScH_2. We observe minima ranging from 6 to 8 msec. In practice we normalize (1) in order to determine τ for each T_1. Results of these calculations are shown in Figs. 2–4.

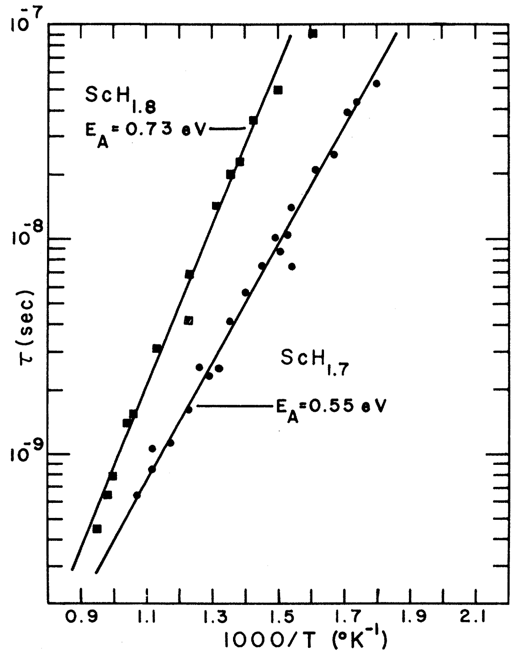

FIG. 2. Temperature dependence of hydrogen jump time for $ScH_{1.7}$ and $ScH_{1.8}$.

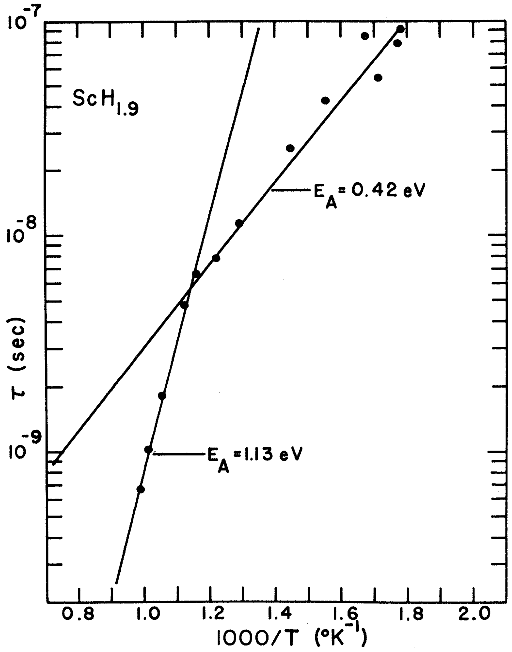

FIG. 3. Temperature dependence of hydrogen jump time for $ScH_{1.9}$.

B. Rigid-Lattice Linewidth

The second moments of the hydrogen line were determined by numerically integrating the resonance-absorption profile.[7] The results for room temperature are shown in Fig. 5. A calculation of the second moment is complicated by having the possibility of hydrogen being located in two inequivalent sites[1] and by the presence of a metal spin from which an appreciable contribution to the moment is found. The essential arguments are given by Stalinsky *et al.*[12] The observed second moment is given by

$$M_2 = f_t M_2^{(t)} + f_0 M_2^{(o)}\ , \qquad (4)$$

where f_t represents the fraction of spins in a tetrahedral or octahedral site and $M_2^{(t)}(M_2^{(o)})$ is the second moment for tetrahedral (octahedral) sites. Using the Van Vleck relation[7, 13] we have

$$M_2^{(q)} = \tfrac{3}{5} C_I(\alpha_t S_{qt} + \alpha_o S_{qo}) + \tfrac{4}{15} C_S \alpha_m S_{qm}\ , \qquad (5)$$

where I and S refer to proton and metal spins, respectively. The quantities α_j represent the probability of occupation for the respective sites and S_{ij} is the sum $\sum r_k^{-6}$ in which the origin is located at an i site and summations extend over sites of type j. We note

$$f_t = 2\alpha_t/(2\alpha_t + \alpha_o)\ ,\quad f_o = \alpha_o/(2\alpha_t + \alpha_o)\ , \qquad (6)$$

and

$$x = 2\alpha_t + \alpha_o\ , \qquad (7)$$

where x is the hydrogen-to-metal ratio. Combining these relations we have

$$M_2 = \tfrac{3}{5}(C_P/x)[2\alpha_t^2 S_{tt} + \alpha_t\alpha_o(2S_{to} + S_{ot}) + \alpha_o^2 S_{oo}]$$
$$+ \tfrac{4}{15}(C_m/x)(2\alpha_t S_{tm} + \alpha_o S_{om})\ . \qquad (8)$$

In Fig. 5, we have plotted the results of Eq. (8) for several assumed configurations. Should the numbers be taken at face value, one would conclude that a few percent of the hydrogen are located in the octahedral sites and this number remains roughly constant as the concentration increases. Actually, the data do not unambiguously distinguish between configurations, but we can probably exclude the possibility of having a constant number of tetrahedral atoms (α_t) with the octahedral number varying with x.

IV. DISCUSSION

The most unusual aspect of our data is the marked deviation of $\tau(T)$ from a single exponential. Con-

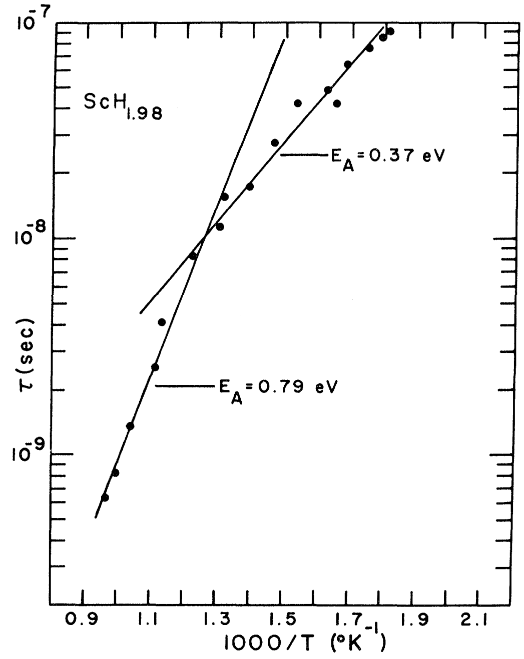

FIG. 4. Temperature dependence of hydrogen jump time for $ScH_{1.98}$.

tributions to T_1 from electron-nuclear interactions normally are associated with such behavior. However, in the present case the break from exponential dependence occurs at a temperature near the minimum for T_1. Although there might be a 10% contribution to T_1 from nondiffusion mechanisms, an effect of this size is hardly adequate to induce a change in slope of the magnitude observed. Furthermore, the sudden change in character for data from $ScH_{1.8}$ to $ScH_{1.9}$ is inconsistent with the usual interpretation for electronic behavior for single-phase hydrides in which bands gradually fill[5] or continuously move[6, 14] relative to the Fermi level as the hydrogen concentration changes. More likely, the increased slope at higher temperatures is a consequence of a change in nature of the activation process.

A change in slope for $\tau(T)$ could simply reflect a temperature dependence for E_A. However, it is not uncommon to observe multiple activation energies for proton motions.[3, 10] For the present situation there is a very simple second-diffusion mechanism which offers an attractive explanation for our observations.

Scandium dihydride is cubic (CaF_2) and consists of metal atoms located on a fcc lattice with the hydrogens positioned at interstitial sites with tetrahedral symmetry. Although a second-type interstitial site with octahedral symmetry exists, there is theoretical[15, 16] and experimental[3, 14] evidence that the tetrahedral site lies lower in energy and, consequently, is preferentially filled. These considerations indicate that proton diffusion occurs primarily by means of vacancy motion between tetrahedral sites.

A different migration mechanism occurs by the formation of a vacancy-interstitial pair relative to the sublattice of tetrahedral sites. Such a configuration results when a tetrahedral atom moves into an octahedral site. The formation of these defects is favored for higher hydrogen concentrations. Since jumps to octahedral sites are energetically less favorable than jumps to empty tetrahedral sites, it is not unreasonable to speculate that this type of motion is responsible for the nonexponential behavior of $\tau(T)$.

For the moment, consider the implications of identifying two processes in the $\tau(T)$ plots for $ScH_{1.9}$ and $ScH_{1.98}$. The lower value of E_A from these samples must be identified with tetrahedral-to-tetrahedral jumps, since the defect-pair formation requires more energy.[17] Thus, the activation energy for t-t motion $E_A(T)$ shows an initial increase as x increases, followed by a monotonic decrease for $x > 1.8$. It is generally found that this parameter either remains constant or slightly decreases as x approaches 2, an effect which is probably due to proton-proton interactions.[3] We also note that the magnitude of the change in E_A for $x > 1.8$ is consistent with an appreciable population of the octahedral sites when using a screened-ion interatomic potential such as described in Ref. 18.

The observed increase for E_A upon increasing x from 1.7 to 1.8 is unusual for transition-metal hydrides. Since simple models for interatomic potentials indicate either a decrease[3] or a very

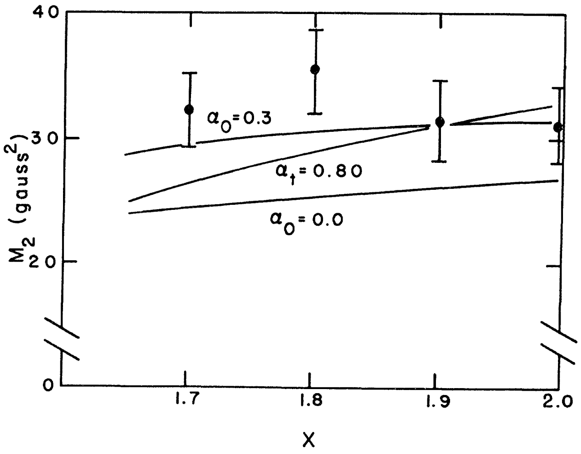

FIG. 5. Experimental proton second moment as a function of concentration. The solid lines are from calculations of M_2 in which the probability of occupation for either octahedral (α_0) or tetrahedral (α_t) sites is held constant.

small increase,[18] we can only suggest that this measurement reflects a change in the electronic band structure. It is possible to argue at least speculatively that an increase in E_A is expected from the band-structure work. These calculations indicate that as x increases, the hydrogen bands, as well as the metal S band, drop relative to the Fermi energy.[6] This action tends to decrease the S character of the conduction electrons. As a result of their isotropic nature, the S-state electrons are probably better at screening the charged ions. If it is true, the smaller amount of S character leads to a decreased screening effect. A reduction in screening would increase the Coulomb interaction between ions leading to a larger E_A.

Finally, we observe that while there is no straightforward connection between E_A and the electronic band structure, we would expect unidirectional variation with x for rigid-band filling. Thus, there appears to be no simple way to account for these data using such considerations.

V. CONCLUSIONS

Concentration-dependent activation energies were observed for hydrogen diffusion in ScH_x. This behavior does not support a rigid-band model. Appreciable population of octahedral positions is indicated by both rigid-lattice linewidth and the concentration dependence of activation energies.

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