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NMR study of thorium hydrides (Th_4H_{15}, ThH_2) and deuteride (Th_4D_{15})

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Thorium hydride was studied using NMR techniques. Relaxation times of protons and deuterons inTh_4H_{15} and Th_4D_{15} were measured over a wide temperature range. Different diffusion processes in different temperature regions were observed. In the range $417 \lesssim T(°K) \lesssim 526$ the activation energy for hydrogen (or deuterium) diffusion was calculated to be $E_a \simeq 14.7$ kcal/mole. The preexponential factor τ_0 was calculated to be $\tau_0 \simeq 10^{-14}$ sec for hydrogen, and $\tau_0^D \simeq \sqrt{2}\tau_0^H$ for deuterium. The frequency of the quadrupole interaction of the deuterons ν_Q was found to be in the range $37.4 \lesssim \nu_Q \lesssim 43.2$ kHz. The electronic contribution to the relaxation in samples of ThH_2 and Th_4H_{15} was calculated from spin-lattice relaxation-time measurements at low temperatures ($78 \leq T \leq 300$ °K). While in ThH_2 this contribution can be given as $(T_1T)_e = 567 \pm 30$ sec °K in the above temperature range, that of Th_4H_{15} has been found to be temperature dependent. Analysis of this temperature dependence and that of the Knight shift (measured by Lau *et al.*) permitted an estimation of the hyperfine fields of the *s* and *d* electrons at the site of the proton. In view of the NMR results it is suggested that *f* electrons are not present in a significant amount on the Fermi level.

INTRODUCTION

Thorium hydride, Th_4H_{15}, has recently attracted considerable attention, especially due to its interesting superconducting properties. Its transition temperature $T_c \simeq 8$ °K is the highest found for a metal hydride which is stable at room temperature. Previous NMR studies of the hydride system did not give consistent results.[1-3] In the present study both the hydride and deuteride systems were investigated over a wide temperature range. The results of this study give new information about the diffusion process and the electronic structure of these compounds. In light of our findings we suggest an explanation of the dependence of T_c on the method used to prepare Th_4H_{15}.[4] The spin-lattice relaxation time measured by us differs from that found previously[1-3] and its temperature dependence is compatible with the Knight-shift temperature dependence measured by Lau *et al.*[1]

It was previously proposed[5-7] that *f* electrons are present on the Fermi level in this compound. Our results do not seem to support this view.

EXPERIMENTAL DETAILS

Two samples of the Th_4H_{15} phase were prepared. One contained the maximum amount of hydrogen, with a H/Th ratio of 3.75, and will be designated $ThH_{3.75}$. The other was a hydrogen-deficient sample with a H/Th ratio of 3.5 and will be designated $ThH_{3.5}$. A sample of the lower phase of thorium hydride ThH_2 was also prepared in order to compare its NMR properties with those of the higher phase. This phase has a different crystallographic structure and is not a superconductor. A sample of Th_4D_{15} was also synthesized and characterized as $ThD_{3.7}$. The method of hydride preparation was similar to that described by Lau *et al.*[1] for their sample *A*, where no especially high pressure or temperature was employed. The error in the amount of hydrogen absorbed by the metal samples was ±1%. The superconducting transition temperature of both Th_4H_{15} samples was found to be ~7 °K.

Relaxation-time measurements were performed using a phase-coherent pulsed-NMR spectrometer, with phase-sensitive detection. Signals were averaged with a Fabritek Model 1070 signal averager combined with a Biomation Model 802 capable of digital counting. Measurements of proton T_1 in the temperature range $300 < T \leq 620$ °K were taken at a resonance frequency of 25 MHz and in the range $78 \leq T \leq 300$ °K, at 19 MHz. Measurements of the deuteron relaxation were taken at 12.8 MHz. Some cw measurements of proton spectra were made using a Varian wideline spectrometer at a resonance frequency of 16 MHz.

T_1 of the protons was measured in the low-temperature region ($T \leq 300$ °K) by applying a saturation comb of 90° pulses, and observing the recovery of the magnetization towards the equilibrium value as a function of time. This method is convenient for measuring relatively long relaxation times, as the first pulse in the pulse train is the 90° measuring pulse and the time between consecutive combs in the averaging sequence is varied in order to obtain the T_1 curve. The time dependence of the magnetization is given by

$$M(t) = M_0(1 - Ae^{-t/T_1}) \ , \tag{1}$$

where M_0 is the equilibrium value of the magnetization and A is a constant which depends on the width of the saturating pulse. For an exact 90° pulse and complete saturation $A = 1$.

In the high-temperature region ($T > 300$ °K) where the values of T_1 are much smaller we used a 180°- τ-90° sequence of pulses. The magnetization curve in this case is also given by Eq. (1), but $A = 2$ for an exact 180° pulse. T_1 was calculated using a nonlinear least-squares-fit program, by which the function of Eq. (1) was fitted to the experimental results. In this fit, A, M_0, and T_1 were free parameters. This avoids the accumulation of the experimental error in M_0, which occurs in a semilog plot method. An illustration of the resulting fit is given in Fig. 1. The average errors in the computed values of T_1 were ~3% for Th_4H_{15} and ~5% for ThH_2 at low temperatures and ~2% in the high-temperature range for all the samples.

The spin-spin relaxation time T_2 was also measured in the $ThH_{3.75}$ sample over the temperature range $480 \lesssim T \lesssim 621$ °K, using the spin-echo method. The average error of these results was ~2%.

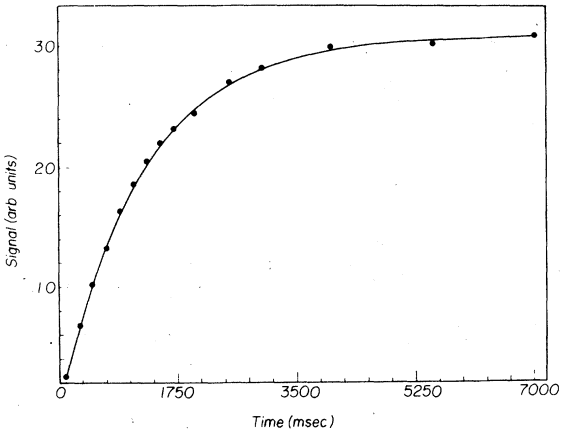

FIG. 1. Typical fit of Eq. (1) to the measured signal as a function of time. The circles represent the experimental results, the solid line the theoretical fit from which T_1 was derived.

A cooled gas-flow cryostat was used for temperature variation. By controlling the flow rate of the cooled nitrogen gas, a temperature stability of ±0.5 °K was reached during each measuring cycle. The sample and the measuring coil were placed inside a copper cylinder to assure good homogeneity and stability of the temperature of the samples. The copper cylinder also served as a rf shield. The sample temperature was monitored by a calibrated platinum resistor. A water-cooled furnace was used to achieve high temperatures. A dc current supply, which was controlled by a pallador II thermocouple, kept the temperature constant within ±0.3 °K. A similar thermocouple was used to detect the sample temperature. The temperature gradient between the sample and the monitoring point was carefully checked and taken into account. The accuracy in the temperature reading was better than 1%.

RESULTS AND DISCUSSION

A. General features of the relaxation times

Figure 2 presents the results obtained for T_1 and T_2 in all the samples. It should be noted that (i) T_1 of ThH_2 is 2.5–3 times longer than that of Th_4H_{15}; (ii) T_1 of the sample $ThH_{3.5}$ is the same as that of $ThH_{3.75}$ at low temperatures but is shorter at room temperature; (iii) there are minima in the T_1 curves of $ThH_{3.75}$ and Th_4D_{15} at $T = 573$ and 560 °K, respectively; and (iv) the shape of these curves is not symmetri-

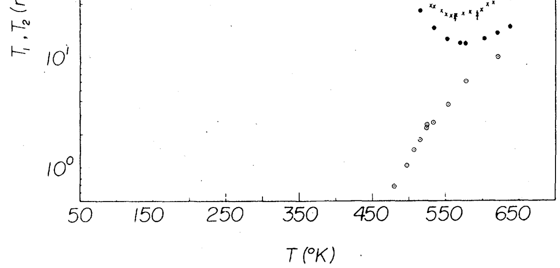

FIG. 2. Spin-lattice relaxation times T_1 of ThH_2, Th_4H_{15}, Th_4D_{15}, and spin-spin relaxation times T_2 of Th_4H_{15}. ⊡ , T_1 of ThH_2; ● , T_1 of $ThH_{3.75}$; △, T_1 of $Th_{3.5}$; ×, T_1 of Th_4D_{15}; ○, T_2 of $ThH_{3.75}$.

cal with respect to the position of the minmum point. This feature is especially clear in the deuteron T_1 curve.

Comparing our T_1 results with those previously published,[1-3] we note that we obtained consistently longer relaxation times. Our values of T_2 almost reach the values of T_1, thus showing that bulk susceptibility[8] has a negligible effect on T_2 in the measured temperature range.

B. Analysis of the high-temperature ($T > 300$ °K) results: Diffusion of H and D

T_1 and T_2 behavior shows clearly that at high temperatures the main mechanism contributing to relaxation is the dipolar (quadrupolar) interaction modulated by hydrogen (or deuterium) diffusion. The well-known equations relating relaxation time with the correlation time τ of the motion of the nuclei are[9]

$$\frac{1}{(T_{1d})^{di}} = \frac{2}{5}\gamma^4\hbar^2 I(I+1) \times \left[\sum_i r_i^{-6}\right]\frac{1}{\omega}p(y) \ , \tag{2a}$$

$$\frac{1}{(T_{1d})^{Q}} = \frac{3}{10}\pi^2\left(1+\frac{1}{3}\eta^2\right) \times \left[\frac{e^2qQ}{h}\right]^2\frac{1}{\omega}p(y) \ , \tag{2b}$$

$$1/T_{2d} = \gamma^2 M_2 \tau \quad \text{for } M_2^{1/2} << 1 \ , \tag{2c}$$

where $(T_{1d})^{di}$ is the diffusion-dependent relaxation caused by dipolar interactions and $(T_{1d})^{Q}$ is that caused by quadrupole interaction. T_{2d} is the spin-spin relaxation time of the protons and M_2 their rigid-lattice second moment. We assume that T_{2d} is given by[8]

$$1/T_{2d} = 1/T_2 - 1/T_1 \ , \tag{3}$$

where T_2 and T_1 are the measured values. In Eq (2), ω is the Larmor frequency, γ is the nuclear gyromagnetic ratio, q is the electric field gradient, Q is the nuclear quadrupole moment, $y = \omega\tau$, and η is the asymmetry parameter. The function $p(y)$ is

$$p(y) = y/(1+y^2) + 4y/(1+4y^2) \ . \tag{4}$$

$p(y)$ reaches a maximum for $y \simeq 0.616$, where its value is $p(0.616) \simeq 1.425$. Using these values, Eqs. (2a) and (2b) can be written in the following form:

$$\alpha = \frac{(T_{1d})^{di,Q}}{(T_{1d}^{\min})^{di,Q}} = 1.425p(y) \ , \tag{5}$$

where $T_{1d}^{\min}$ is the minimum value of T_{1d}. T_{1d} was calculated by subtracting the electronic contribution $1/T_{1e}$ from the measured value of $1/T_1 (1/T_{1d} = 1/T_1 - 1/T_{1e})$. From a universal plot of α vs y, and the experimental values of α, we derive the values of y and hence of τ as a function of $1/T$(°K). Figure 3 presents the calculated values of y vs $10^3/T$(°K), for Th_4H_{15} and Th_4D_{15}. It is seen that the data cannot be well approximated by a single straight line in the whole temperature range, but at least in the region $1.9 \lesssim 10^3/T(°K) \lesssim 2.4$, i.e. $(4.17 \lesssim T \lesssim 526$ °K) the points lie fairly well on such a line. Hence we assume that at these temperatures only one diffusion process is significant and the correlation time obeys the Arrhenius relation $\tau = \tau_0 e^{E_a/RT}$. E_a is the activation energy for diffusion and R is the gas constant. We obtain values for E_a of (14.1 ± 1) and (14.5 ± 1) kcal/mole for Th_4H_{15} and Th_4D_{15}, respectively.

The deviation of the points shown in Fig. 3 from a straight line at high and low temperatures indicates that more than one diffusion mechanism exists. The curvature at low temperatures ($10^3/T$ (°K) $\gtrsim 2.6$) indicates a diffusion having a smaller E_a than at higher temperatures. This is in accord with the finding of Lau *et al.*[1] who found, from $T_{1\rho}$ measurements, an activation energy of 10.9 kcal/mole at these temperatures.

E_a can also be derived from T_2 data. Using Eq. (2c) in the form $\ln(1/T_{2d}) = E_a/RT - \ln B$, in a fit to the experimental values of $1/T_{2d}$, one can obtain the constants E_a and $\ln B$. In Fig. 4 we show such a plot. The values so derived are $E_a = (15.4 \pm 0.5)$ kcal/mole and $\ln B \simeq 8.9$. This value of E_a is in satisfactory agreement with those calculated from the T_1 of Th_4H_{15} and Th_4D_{15}. For further calculations we shall

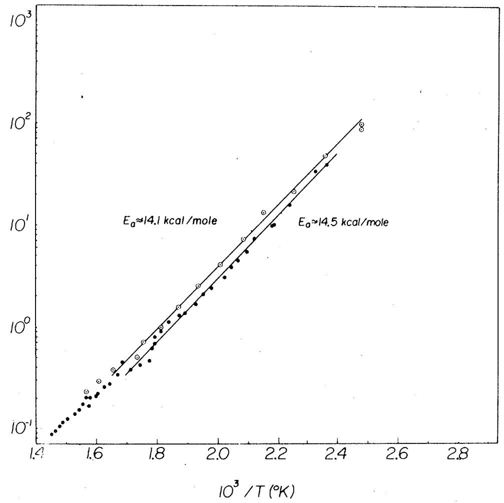

FIG. 3. $y = \omega\tau$ vs $10^3/T$(°K) calculated from T_{1d} results of Th_4H_{15} (⊙) and Th_4D_{15} (●). The resonance frequencies are 25 and 12.8 MHz for the hydride and deuteride, respectively.

use a value of $E_a = 14.7$ kcal/mole. From Fig. 3 we find that the ratio between values of τ for deuterium and hydrogen is very close to $2^{1/2}$. This value is in accord with the simple picture of self-diffusion in which the jump frequency of the atom ν_j is factored as $\nu_j \propto \nu_0 e^{-E_a/RT}$. Here ν_0, the "attempt frequency," is usually identified with the natural vibration frequency of the particle in its potential well.[10]

For diffusion governed by a vacancy mechanism, the jump frequency is sometimes written in the form[11]

$$\nu_j = \nu_0 e^{s/k} e^{-E_a/RT} \quad . \tag{6}$$

Here $e^{s/k}$ is an entropy change factor due to vacancy formation and the jump of the atoms. E_a is interpreted as being the sum of the energy of vacancy formation and atom migration. The relation between ν_j and the correlation time τ is given by $\nu_j = 1/2\tau$,[12] and so one obtains

$$\nu_j = (1/2\tau_0) e^{-E_a/RT} \quad . \tag{7}$$

From the calculated values of τ for H in$ThH_{3.75}$ we obtain $\tau_0 \simeq 10^{-14}$ sec. By using a value of $\nu_0 = 3 \times 10^{13}$ Hz derived by inelastic neutron scattering,[13] one gets a value for $s/k \simeq 0.5$.

Another quantity which may be calculated from the T_1 results is the quadrupole interaction of D in Th_4D_{15}. Using Eq. (2b) and the measured value of $(T_{1d}^{\min})^Q \simeq 23$ msec, we get $(1 + \frac{1}{3}\eta^2)^{1/2} \nu_Q \simeq 43.2$ kHz, where $\nu_Q = 3e^2qQ/2h$. For $0 \lesssim \eta \lesssim 1$ we obtain $43.2 \geqslant \nu_Q \geqslant 37.4$ kHz. The deuterium quadrupole interaction is caused by the noncubic local symmetry at the deuterium sites. This noncubic symmetry stems from the crystal structure of Th_4H_{15} and, possibly, vacancies in the deuterium sublattice. The quadrupole interaction was derived from T_1 measurements at high temperatures, where the T_1 is affected by deuterium vacancy diffusion. A typical quadrupole interaction caused by vacancies of deuterium in a cubic stucture was found to be $\nu_Q \simeq 10$ kHz in TiD_x.[14] The higher value found for Th_4D_{15} could be the result of the combination of deuterium vacancies and a noncubic crystal structure.

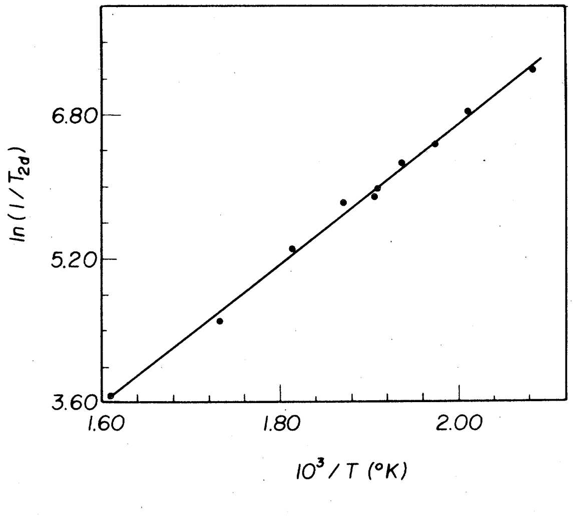

FIG. 4. $\ln(1/T_{2d}) \equiv \ln(1/T_2 - 1/T_1)$ vs $10^3/T$(°K) of Th_4H_{15}. The solid line is a theoretical fit using Eqs. (2c) and (3), by which E_a and $\ln B$ were calculated (see text).

When several diffusion processes exist simultaneously, the correlation time is given by $1/\tau = \sum_i 1/\tau_i$, where τ_i is the correlation time associated with one diffusion channel. Using this relationship we may try to separate the two correlation times which, according to our assumption affect diffusion at temperatures close to room temperature. Writing $1/\tau = 1/\tau_1 + 1/\tau_2$, extrapolating from high temperatures for $\tau_1 \simeq 10^{-14} e^{14.7/RT}$ and using values of τ from Fig. 3 we can calculate τ_2. Assuming further that τ_2 as a function of T is given by $\tau_2 = \tau_{2,0} e^{E_{a_2}/RT}$ and using $E_{a_2} = 10.9$ kcal/mole according to Ref. 1, we get $10^{12} > 1/2\tau_{2,0} \geqslant 10^{11}$ Hz. This value is lower by about two orders of magnitude than the values obtained for hydrogen diffusion in most stoichiometric metal hydrides, and also lower than ν_0. One can speculate that in Th_4H_{15} at low temperatures, hydrogen diffuses through intrinsic vacancies whose concentration (C_0) is about 1% and is independent of temperature. The jump rate in such a model is given by $\nu_j \simeq \nu_0 C_0 e^{-E_{a_2}/RT}$. Thus for $C_0 \approx 10^{-2}$ we get the low value of $1/2\tau_{2,0}$. It is seen in Fig. 5(a) that a narrow line is superimposed on the broad main line of $ThH_{3.75}$. The integrated intensity of the narrow line is estimated to be ~1% of the broad line. Such narrow lines were detected in several hydrides[15] and attributed in some cases to free hydrogen trapped in voids and cracks in the crystallites of the sample. It may be concluded that this is the "missing" hydrogen in the lattice of $ThH_{3.75}$ and that a concentration of about 1% vacancies exists in the lattice even at low temperatures. It should also be remembered that there is quite a large variation in the T_c of different Th_4H_{15} samples (7–9 °K) and that special heat and pressure treatment must be employed while producing the hydride samples in order to reach a high T_c.[4] We think that such treatment helps to fill these vacancies and results in the high T_c form of Th_4H_{15}. This situation is somewhat similar to that of PdH, where by adding an additional small amount of hydrogen by special means, a large increase in T_c is obtained.[16] It is frequently found in superconductors that T_c is sensitive to deviation from local order, which may be caused by vacancies in the crystal.

The curvature of the plot of $\omega\tau$ vs T (Fig. 3) at temperatures higher than the temperature of the minimum in T_1 is not well understood. It might be thought that an additional diffusion mechanism be-

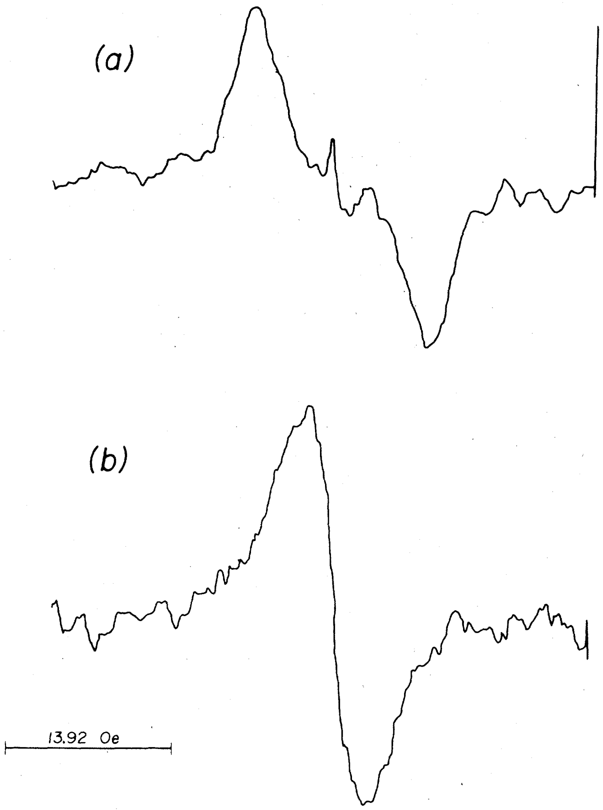

FIG. 5. Derivatives of NMR absorption lines of (a) $ThH_{3.75}$, and (b) $ThH_{3.5}$ at room temperature. The resonance frequency is 16 MHz.

comes important in this temperature range. But an additional diffusion channel should shorten the τ's, while here they seem to become longer than the values extrapolated from lower temperatures. As was remarked previously the shape of the T_1 curve is not symmetrical around the minimum. Wolf,[17] for example, predicts an asymmetric shape for a combined mono-divacancy diffusion mechanism, but the asymmetry here is in the opposite direction. The possibility of a large change in the electronic contribution can also be ruled out. Such a change, while it might be significant in the hydride, would be very small in the deuteride, as $1/T_{1e} \propto \gamma^2$. The behavior of T_1 could be explained by assuming a temperature dependence of E_a. It should be mentioned that Lau *et al.*[1] found evidence of a phase transition at high temperatures in a sample of Th_4H_{15} which was prepared under high hydrogen pressure and high temperature. The change in diffusion found by us could be related to this transition.

Our results showed a difference in the T_1 values at room temperature of $ThH_{3.5}$ and $ThH_{3.75}$. A similar effect of shortening of T_1 in a hydrogen-deficient sample was found in a previous work on UH_3.[18] It was shown that the presence of a metallic phase in the hydride enhances diffusion and thus shortens T_1 at lower temperatures than in a stoichiometric sample. It is seen in Fig. 5 that the linewidth of the protons in sample $ThH_{3.5}$ is almost three times smaller than that of $ThH_{3.75}$ at room temperature. It is concluded therefore, that an effect similar to that in UH_3 is present in Th_4H_{15}. This also explains the discrepancy between the E_a values obtained by Will[19] and those reported by Lau *et al.*[1] and in the present work. Will used samples of Th_4H_{15} in which the H/Th ratio was 3.5.[3]

C. Low-temperature results. Electronic contribution to the relaxation

Figure 6 shows the values of $(T_1T)^{-1/2}$ as a function of T °K in samples of Th_4H_{15} and ThH_2. It can be seen that for ThH_2 the behavior of the relaxation rate can be expressed as $(T_1T)^{-1/2} \simeq 42 \times 10^{-3}$ $(\sec{}^\circ K)^{-1/2}$ (or $T_1T \simeq 567$ sec °K), and is constant in the measured temperature range. However, $(T_1T)^{-1/2}$ in Th_4H_{15} is not constant as a function of temperature. For the sake of comparison with previously published results[1-3] we give our values of T_1T of $ThH_{3.75}$ at the two extreme temperatures: $T_1T \simeq 165$ sec °K at 78 °K, and $T_1T \approx 230$ sec °K at 300 °K. This change of T_1T is much larger than the experimental error. The variation of $(T_1T)^{-1/2}$ is quite similar to that of the Knight shift, measured by Lau *et al.*[1] When K and T_1T have been found to be temperature dependent in nonmagnetic materials, it has usually been explained as being due to the sharp structure of the density of states function on the Fermi level E_F.[20]

The NMR results of this study and those of Lau *et al.* may be explained by assuming a hyperfine interaction of the protons with the electrons of the d and s bands.[21] The existence of f-type conduction electrons in Th_4H_{15} was suggested by Dietrich *et al.*[5] on the basis of the measured pressure dependence of T_c. This was also proposed by Miller *et al.*,[6] who found from heat-capacity measurements, a larger density of states than reported elsewhere.[22] A calculation of partial densities of states in Th_4H_{15} and ThH_2 was carried out by Winter and Ries.[7] Their results predict

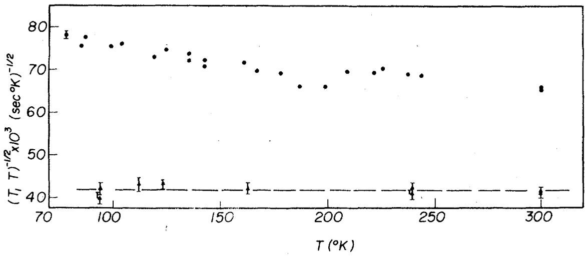

FIG. 6. $(T_1T)^{-1/2}$ vs T(°K) in samples Th_4H_{15}(●) and ThH_2 (▲)

a large f contribution to the conduction band. Moreover, the f-band density of states function has a positive and almost infinite derivative at the Fermi level. Two objections can be raised against this model. First, the total calculated value of the density of states at E_F is by far larger than that derived from heat-capacity measurements.[6] Second, the steep rise of the f band at the Fermi level should manifest itself in the NMR quantities (K and T_1T) in a way different from the one observed. The "broadening" of the Fermi-Dirac distribution with increasing temperature should give more "weight" to the rising f band and therefore increase the relaxation and Knight shift, contrary to the experimental findings. Hence, it seems that, near the Fermi level, the conduction band is mainly composed of a high d band, which has a sharp structure in the vicinity of E_F and a low broad s band. This assumption is in agreement with NMR results and, also, the density-of-states value estimate of the d and s bands of Winter and Reis[7] is close to the experimental one.[6] With the above assumption one can write the following expression for the relaxation rate[23]:

$$\begin{aligned} 1/(T_1T)_e = \pi\gamma^2\hbar k_B |H_{\rm hf}^{(s)} N_s(E_f)|^2 \\ + |H_{\rm hf}^{(d)} N_d(E_f)|^2 q \\ + |H_{\rm hf}^{(0)} N_d(E_f)|^2 p \ , \end{aligned} \tag{8}$$

where $1/(T_1T)_e$ is the conduction electrons contribution to the relaxation rate, divided by the absolute temperature; $N_s(E_f)$ and $N_d(E_f)$ are the densities of states of the s and d electrons at the Fermi level; and $H_{\rm hf}^{(s)}$, $H_{\rm hf}^{(d)}$, and $H_{\rm hf}^{(0)}$ are the hyperfine fields of the s contact, the d-core polarization, and d-orbital interactions, respectively. p and q are the reduction factors. In Eq. (8) a simplification is made by neglecting a possible s-d mixing term. Also the meaning of the core-polarization term is here different from its usual meaning. We assume the existence of an indirect interaction between the protons and the d-conduction electrons of the thorium atoms. This may be brought about by an exchange interaction between these d electrons and s electrons localized on the protons. In view of the large variation of the Knight shift and its leveling off above 200 °K and the similarity in the temperature dependence of K and $(T_1T)^{-1/2}$ (see Fig. 8 in Ref. 1) we assume that the orbital term is negligible in both the shift and the relaxation.

We may therefore write the Korringa-like relations[23]

$$\frac{1}{(T_1T)_s} = \frac{4\pi k_B}{\hbar}\left(\frac{\gamma_n}{\gamma_e}\right)^2 K_s^2 \ , \tag{9a}$$

$$\frac{1}{(T_1T)_d} = \frac{4\pi k_B}{\hbar}\left(\frac{\gamma_n}{\gamma_e}\right)^2 K_d^2 q \ , \tag{9b}$$

where K_s and K_d are the contact and core-polarization terms of the Knight shift, and $(T_1T)_s$ and $(T_1T)_d$ are the corresponding contributions to $(T_1T)_e$. The magnitude of the variation in the Knight shift is different from that of $(T_1T)^{-1/2}$. In the temperature range 78–300 °K, $(T_1T)^{-1/2}$ varies by ~15%, while the measured Knight shift changes by approximately a factor of 4. In order to estimate the different contributions to K we assume that at room temperature the main contribution to the interaction is due to the s electrons. This assumption is based on the fact that $T_1T)_e^{-1/2}$ and the Knight shift are almost constant at temperatures close to 300 °K. We therefore put $(T_1T)_s \simeq 240$ sec °K. Using Eq. (9a), this value gives $K_s \simeq 30$–35 ppm. The possibility of the existence of a chemical shift should also be taken into account. An estimate of nearly −30 ppm of this shift was given by Lau *et al.*[1] Such a chemical shift, which is temperature independent, may cause an almost exact cancellation of K_s. It thus seems that the measured K is approximately equal to K_d alone. Subtracting from the measured $(T_1T)^{-1}$ the above estimated $(T_1T)_s$ [in the form $1/(T_1T)_e - 1/(T_1T)_s$] gives us $(T_1T)_d^{-1/2}$ which is the contribution of d electrons to $(T_1T)_e^{-1/2}$. The fact that the variation of $(T_1T)_d^{-1/2}$ is exactly the same as that of K_d (Fig. 7) indicates that the separation of the s and d contributions to $(T_1T)_e$ is not entirely arbitrary.

An estimation of the s electron hyperfine field can be made with the assumption that $N_s(E_f) << N_d(E_f)$. The total density of states is ≃12–13 states/(Ry atom).[6] We put $N_s(E_f) \simeq 1$–2 states/(Ry atom), as estimated by Winter and Ries.[7] Inserting this value and $(T_1T)_s \simeq 240$ sec °K into the s part of Eq. (8), we get $\zeta = H_{\rm hf}^{(s)}/H_{\rm hf}^{A} \simeq 0.2$–0.5. Here $H_{\rm hf}^{A}$ is the hyperfine field for the free hydrogen atom. Using Eq. (9b) and the values of K_d and $(T_1T)_d$ we calculate the reduction factor to be $q = 0.3$–0.4. Inserting this value, in the d part of Eq. (8), together with the value $N_d(E_f) \simeq 11$ states/(Ry atom) and the value of $(T_1T)_d$ at 78 °K, we get $H_{\rm hf}^{(d)} \simeq 8$ kOe. This $H_{\rm hf}^{(d)}$ is opposite in sign and smaller by one to two orders of magnitude than hyperfine core-polarization fields in many metals.[23] The explanation of this is that the interaction here is a transferred hyperfine interaction, where the electrons producing the hyperfine field at the proton site belong to the neighboring thorium atoms. A similar situation exists in TiH_x,[21]

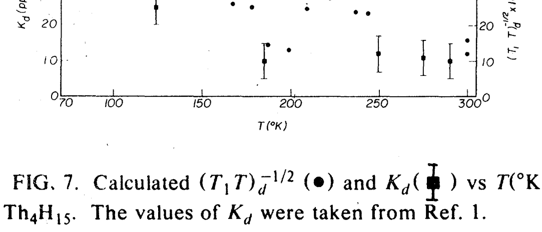

FIG. 7. Calculated $(T_1T)_d^{-1/2}$ (●) and K_d (Ɪ) vs T(°K) of $\mathrm{Th_4H_{15}}$. The values of K_d were taken from Ref. 1.

where hyperfine fields of the same order of magnitude were found. It should be mentioned that a temperature-dependent paramagnetic susceptibility was found for $\mathrm{Th_4H_{15}}$. Although this is qualitatively in agreement with the measured K and $(T_1T)_e^{-1/2}$, we do not use this data quantitatively because detailed results are not yet available.[24]

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