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NMR study of the plutonium hydride system

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An NMR study was conducted on protons in the nonstoichiometric plutonium hydride system, PuH_x. The following compositions were studied: $x = 1.78$, 2.35, 2.65, and 2.78. The line shapes, Knight shifts (K), spin-spin relaxation times (T_2), and spin-lattice relaxation times (T_1) were measured in the temperature range of 77–300 K. The results indicate the existence of paramagnetic phases at high temperatures, with localized $5f$ moments on the Pu ions, and possible magnetically ordered phases at low temperatures. The predicted transition temperatures and type of magnetic order were found to depend strongly on the hydrogen concentration. Different line shapes and shifts are found for the tetrahedral and octahedral protons, which indicate a different bound state for the hydrogen ions. The hydrogen self-diffusion constants were derived from T_2 measurements in the motionally narrowed regime, and were found to be quite similar to those found in the LaH_x system. $T_1 T$ as well as $(K-K_0)^{-1}$ were found to be linear with temperature. The proportionality constants were found to be composition independent. The possible magnetic couplings between the protons and the paramagnetic moments are discussed.

I. INTRODUCTION

The rare-earth hydrides have been studied[1] quite extensively. They usually have metallic conductivity and are magnetically ordered at low temperatures. At high hydrogen concentrations, they seem to become semiconducting, and no indication of magnetic ordering was found at temperatures down to 4 K.[2] This relation between the magnetic and electric behavior seems to indicate that the dominant magnetic coupling interaction involves the indirect exchange via the concuction electrons, sometimes referred to as the Ruderman-Kittel-Kasuya-Yosida (RKKY) type.[3] As pointed out by Fradin,[4] NMR is a useful tool in the investigation of actinide compounds of this type. In the present paper, we report a study on the plutonium hydride system, which is isostructural to the heavy-rare-earth hydrides.

Plutonium dihydride is formed for nominal hydrogen concentration $C_{\mathrm{H}}/C_{\mathrm{Pu}} \leq 2$ with the fluorite-type structure. This structure has a face-centered-cubic metal sublattice, with hydrogen ions in the tetrahedral positions, and a lattice constant of 5.359 Å. Hydrogen excess compositions up to $C_{\mathrm{H}}/C_{\mathrm{Pu}} \approx 2.75$ are due to hydrogen atoms in the octrahedral interstices of the lattice.[5] In this region, as the hydrogen concentration increases, the lattice parameter decreases down to 5.34 Å.[6] At higher hydrogen concentrations, the hydride partially undergoes a first-order phase transition to a hexagonal structure. The hexagonal trihydrides can be hydrogen deficient with a relatively wide range of stoichiometry.

Olsen *et al.*[7] found, in $\mathrm{PuH}_{2.74}$, a ferromagnetic phase transition at 107 K. The present study provides some information on the magnetic coupling between the protons and the paramagnetic moments of the plutonium ions. The magnetic interactions in such systems may be quite helpful in investigating differences between the tetrahedral and octahedral hydrogen atoms.

II. EXPERIMENTAL TECHNIQUES

The hydrides were prepared by direct reaction of a known amount of hydrogen gas with a known weight of plutonium metal. The brittle hydrides were crushed to powder inside the hydrogenation system, without exposing the material to the external atmosphere, and sealed in glass capsules with some helium exchange gas. The samples were then heated for several hours to improve the hydrogen concentration homogeneity. The composition is believed to be accurate to ~1%. We used a pulsed NMR spectrometer, and most measurements were carried out at 22 MHz. Some details concerning the experimental techniques and the data analysis are described in a previous article.[8] The maximum relative error in T_1 is ~3%. The sample temperature accuracy is ~2%, and its stability was better than 0.3 °C.

Some of the line shapes were derived from the free-induction-decay (FID) signal using a boxcar integrator and sweeping the external magnetic field. This technique gives accurate line shape as long as the integration interval t_1 to t_2 is in the range $t_1 \ll \tau_2 \ll t_2$, where τ_2 is the FID time constant. Otherwise, the derived line shape may contain artificial field-dependent oscillations. When the broadening was of an inhomogeneous type, and T_2 was not too short, we integrated the spin echo signal. The line shapes of the very broad lines are accurate, as long as the rf field H_1, which was ~60 G, is small compared with the variations of the spectral line. In this case, the shape will be an absorption type, regardless of the reference phase of the detector.

III. RESULTS

A. Line shapes and T_2

The line shape of the protons is determined mainly by the crystallographic structure, atomic motion, and magnetic interactions. We have measured the line shapes of all samples from room temperature to 77 K.

The line shape of $PuH_{1.78}$ was measured at 22 MHz in the temperature range of 77–300 K. No changes were noted to within the experimental error, which was ~1%, and no inhomogeneous broadening was observed. The FID was a Gaussian shape with $T_2 = 17.5 \mu sec$. The second moment of this line is equal to $M_2 = \pi/2\gamma^2 T_2^2 = 7.2$ Oe^2. This value is in good agreement with the calculated value, assuming a dipolar proton-proton interaction (Van Vleck second moment), for a rigid lattice of protons located at tetrahedral sites.

The temperature dependence of the line shape in $PuH_{2.35}$ behaves in an entirely different manner. At room temperature, the line is motionally narrowed as a result of proton diffusion and has the expected Lorentzian shape. At approximately −80 °C, the line shape corresponds to a rigid lattice and, at lower temperatures, the rigid line becomes inhomogeneously broadened. This broadening increases as the temperature decreases and is characteristic of paramagnetic broadening. At low temperatures, the line becomes somewhat asymmetric with the longer wing on the lower-field side, as can be seen in Fig. 1. At 77 K, $T_2 = 21 \mu sec$, and the corresponding homogeneous component of the line has a Lorentzian shape, which is in contrast to the expected nearly Gaussian shape in rigid lattices. This Lorentzian shape is common to all plutonium hydrides, except the dihydride. It might be the result of some decoupling of the dipolar interaction due to the paramagnetic broadening.

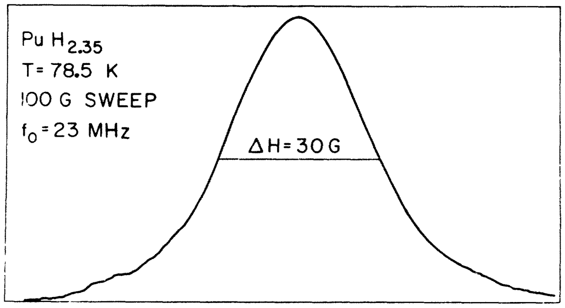

FIG. 1. Absorption line of $PuH_{2.35}$ at 23 MHz and 78.5 K. Field increases to left.

The line shape of $PuH_{2.65}$ is more complicated. At high temperatures, the line is motionally narrowed. At low temperatures, two inhomogeneous broadened lines are found, as is seen in Fig. 2. At 83 K, the more intense line is shifted to lower fields by an amount $(4.6 \pm 0.1) \times 10^{-3} H_0$, where H_0 is the unshifted line position. The weaker line was found to have a negligible Knight shift within our experimental error. The spin-lattice relaxation times T_1 of the two lines were measured and found to be equal. This is expected if both lines correspond to protons of the same phase, as a result of their mutual cross relaxation, which in this case is much shorter than T_1. The ratio of the integrated areas of the lines is equal to the ratio of the number of octahedral to tetrahedral protons, namely, 0.65 to 2. We therefore associate the intense line with the tetrahedral protons and the smaller line with the octahedral protons. In the intermediate temperature range, these two lines are still distinguishable. The FID signal at 148 K is shown in Fig. 3. The amplitudes of the two components have the correct relative magnitude, corresponding to the protons population in the two different sites. It is interesting to point out that, in this temperature range, only the octahedral proton line is motionally narrowed, i.e., at this temperature, the diffusion rate of the octahedral proton is faster than that of the tetrahedral protons. At 83 K, the homogeneous portions of the rigid-lattice lines have a Lorentzian

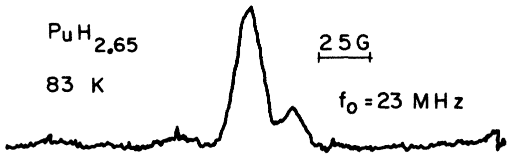

FIG. 2. Absorption line of $PuH_{2.65}$ at 23 MHz and 83 K. Field increases to right.

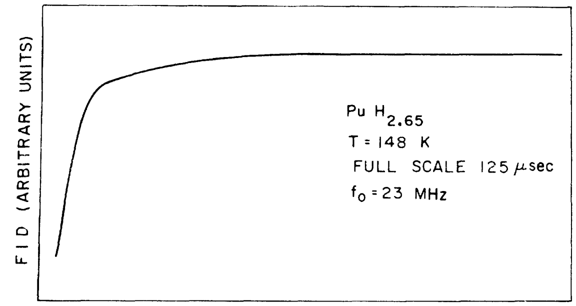

FIG. 3. Free-induction decay of $PuH_{2.65}$ at 23 MHz and 148 K. Time scale: 125 μsec full scale.

shape, with $T_2 = 17\mu$sec for the octahedral line and 19 μsec for the tetrahedral line.

The temperature dependence of the $PuH_{2.78}$ spectrum is similar to that of $PuH_{2.65}$. At room temperature, only the octahedral line is motionally narrowed, whereas the other is partially broadened. At lower temperatures, the inhomogeneous broadening of the spectrum becomes quite large, as can be seen in Fig. 4. Both the broadening and the shift of the tetrahedral line are much larger than those of the octahedral line. Below ~91 K, a new broad line appears. At 77 K this line is centered at ~1100 G for a Larmor frequency of 23 MHz. This shift corresponds to an internal field of ~4300 G. The area of this line increases gradually as the temperature decreases, at the expense of the other (paramagnetic) lines. Such temperature dependence can be expected only for an NMR line in the magnetically ordered phase. This is confirmed quantitatively by the present Knight-shift measurement in the paramagnetic phase and by some preliminary magnetic measurements. The line shape of the homogeneous portions at 109 K, was found to be Lorentzian with $T_2 = 16.5$ μsec.

T_2 was measured in the conventional 90°-τ-180° pulse sequence, and the results are given in Fig. 5. At room temperature where the lines are motionally narrowed (except for $PuH_{1.78}$), T_2 does not approach T_1. This discrepancy results from the effect of the macroscopic magnetic field inhomogeneity, inside each sample grain, when the proton diffusion is too fast.[9] One can overcome this effect by using the Meiboom-Gill sequence.[10] Nevertheless, in the intermediate temperature range, our results are sufficiently accurate to evaluate the diffusion activation energy E_a and to obtain a rough estimation of the preexponential factor ν_0 of the diffusion rate ν_{dif}, where $\nu_{dif} = \nu_0 e^{E_a/RT}$. The proton-proton dipolar correlation time τ_c is equal to $1/2\ \nu_{dif}$. The factor 2 results from the contribution of the neighboring proton jumps to the fluctuations in the dipolar interaction of the observed proton.[11] Hence, the motionally narrowed line is given approximately by

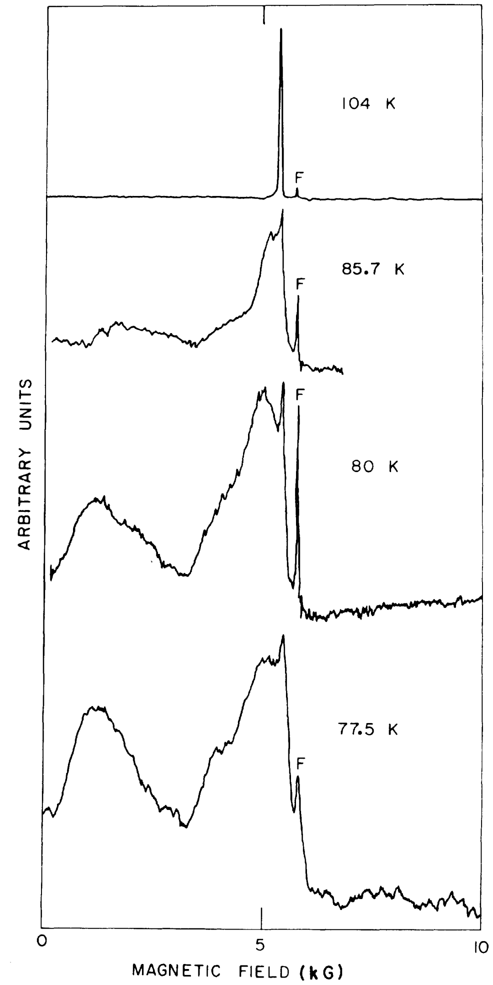

FIG. 4. Absorption spectra of $PuH_{2.78}$ at 23 MHz. F indicates the flourine line of the sample capsule.

$$(1/T_2)_d \approx \langle \Delta\omega_0^2 \rangle \tau_c = (\langle \Delta\omega_0^2 \rangle / 2\nu_0) e^{E_a/RT},$$

where $(1/T_2)_d = 1/T_2 - 1/T_1$, and $\langle \Delta\omega_0^2 \rangle$ is the second moment of the rigid lattice. This approximation is good as long as the linewidth is much smaller than that of the rigid lattice, or equivalently, as long as $T_2 \gg T_2^*$, where T_2^* is the spin-spin relaxation time of the rigid lattice and is, in this system, smaller than 20 μsec. On the other hand, we have avoided the high-temperature range, where T_2 is too long (and the diffusion too fast), because of the uneliminated effect of the macroscopic magnetic inhomogeneity, as was mentioned above. Unfortunately, we cannot use the measured values of T_2^* in this system because of the appreciable exchange narrowing that was

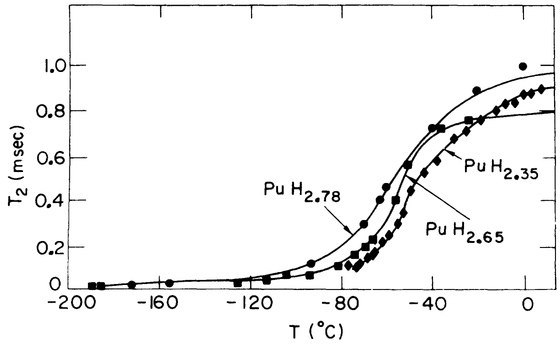

FIG. 5. Temperature dependence of spin-spin relaxation time for different hydrogen concentrations.

observed at the low temperatures. We assume that at the higher temperatures, the exchange narrowing is negligible and hence $\langle \Delta\omega_0^2 \rangle$ approaches the theoretical Van Vleck value. In a least-squares fit, the deduced values of ν_0 are accurate only to an order of magnitude because of the strong T_2 dependence on E_a. The values of E_a and ν_0 deduced under the above assumption are given in Table I.

The linewidth of $PuH_{1.78}$ is entirely due to the rigid-lattice dipole-dipole interaction up to room temperature and no motional narrowing is observed. This feature suggests an increase in the activation energy for hydrogen diffusion compared with the samples of higher hydrogen concentrations. Such a composition dependence of the diffusion constants was also found in the LaH_x system by Schreiber and Cotts.[12] These authors have suggested a model for the proton diffusion that explains semiquantitatively the big change in E_a around $x \approx 2$. Whatever is the true mechanism, it seems that in both systems the protons diffuse in the same manner. The analogy between the systems may be supported by the observation of a narrow line superimposed on a broad one in the intermediate temperatures for LaH_x with $x > 2.5$. Schreiber and Cotts could not measure the exact areas of these lines because they used the continuous-wave technique, but they suggested that the complex line narrowing could be a result of slight differences in activation energies for regions in the lattice around nondiffusive defects, as opposed to those regions relatively free of defects. This is certainly not the case in our system, as can be seen from the large difference in line shifts and the well-defined spectrum. The PuH_x system can coexist in two phases, as was mentioned in Sec. I, whereas the LaH_x system exists only in the cubic form. The appearance of two lines in the spectra of LaH_x (for $x > 2.6$) seems to support our conclusion that the two lines in $PuH_{2.65}$ represent protons in different sites of the same phase. The second moment of a rigid lattice line might be a sensitive indicator of the phase. In the hexagonal phase of PuH_3, the ions are located in the following sites: 2Pu: $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$, $2H_I$: $\pm(0, 0, \frac{1}{4})$, and $4H_{II}$: $\pm(\frac{1}{3}, \frac{2}{3}, Z) \pm (\frac{2}{3}, \frac{1}{3}, \frac{1}{2}+Z)$, where $a = 3.78$ Å, $C_0 = 6.76$ Å, and $Z = 0.607$. We have calculated the second moments of the protons in the different sites and obtained, for the trihydrid,

TABLE I. Diffusion constants for the octahedral protons.

x (H/Pu)	2.35	2.65	2.78
E_a (kcal/mole)	5.5 ± 0.2	6.1 ± 0.5	3.2 ± 0.5
ν_{0c} (10^{11} Hz)	6	11	0.3

$$M_2(H_I) = 224\ G^2$$

and

$$M_2(H_{II}) = 38\ G^2.$$

For Gaussian lines, the values of the spin-lattice relaxation times would be $T_2(H_I) = 3$ μsec and $T_2(H_{II}) = 7.6$ μsec. Unfortunately, the rigid lines of our samples are exchange narrowed, and an accurate quantitative comparison cannot be made, but the small inhomogeneous broadening of the two lines of $PuH_{2.65}$ at 83 K seems to suggest that the exchange narrowing is not sufficient to account for the much longer measured values of T_2, unless the phase is cubic. The inhomogeneous broadening that was found in the low-temperature range, for the hydrides of $x > 2$, could result from three main mechanisms:

(i) The use of powder specimens produces a macroscopic random magnetic field due to demagnetization effects of the powder grains.[13] The linewidth that arises from this effect is proportional to the magnetization, and the absorption line may have an asymmetric shape. It may explain the observed spectra in $PuH_{2.35}$ and $PuH_{2.65}$. It cannot fully explain the spectra of $PuH_{2.78}$ at the low temperatures near the ferromagnetic transition because the two lines that are affected so differently belong to protons which are located macroscopically in identical places.

(ii) Line broadening can result from a dipolar field, which is due to the neighboring paramagnetic ions. This contribution must vanish in the tetrahedral and octahedral sites, regardless of the hydrogen concentration, as long as all plutonium atoms are magnetically equivalent. However, the negligible Knight shift and inhomogeneous broadening of the octahedral line, with respect to the tetrahedral line, may suggest the existence of different paramagnetic moments in the neighborhood of the two kinds of protons.

The indirect mechanism via a RKKY-type interaction may also contribute to the second moment, when the ionic g tensor is anisotropic, and is given according to Ibers *et al.*[14] as $M_2 \sim (g_{11}^2 - g_1^2)A^2$, where A is the contact interaction constant. In the nonstoichiometic hydrides, the symmetry, with respect to other hydrogen ions, is not cubic, and hence the g tensor may be anisotropic.

(iii) Another source of broadening may result from hydrogen distributed inhomogeneously among the sample grains. The larger broadening of the tetrahedral line, in $PuH_{2.78}$, is consistent with its stronger shift dependence on composition. Near the transition temperature, this dependence may be quite strong as can be seen from the gradual appearance of the ferromagnetic line. However, this line appears at the transition temperature that was predicted from our K and T_1 measurements. The gradual increase in the internal, and, hence, in the magnetization as the temperatures decrease, is consistent with the magnetization results of Olsen *et al.*[7]

B. Line shift

The accuracy of defining the position of the NMR lines depends on their width and shape. For the $PuH_{1.78}$ sample the line, although broad, is symmetric down to our lowest temperature. The position of the line center could be determined to within 15 ppm (80 mG). The lines of the other hydrides are motionally narrowed at the high-temperature range, and their location is well defined. At lower temperatures, their line shapes become complicated, as was seen in the previous section, and therefore it is hard to obtain reliable determination of their centroids. In the case of $PuH_{2.65}$ at the intermediate temperatures, the two lines are not sufficiently separated for their position to be determined. At 83 K, the lines are well separated, as can be seen in Fig. 2. The small line has no shift within the experimental error, which is, in this case, 2×10^{-4}. The larger line has a positive Knight shift of $(4.6\pm0.2)\times10^{-3}$. At 295 K, the shift of both lines is $K=-(2.7\pm0.2)\times10^{-4}$. In Fig. 6, the results of $PuH_{2.78}$ mainly represent the shift of the larger line. The results obtained from all samples were found to have a temperature dependence of the form

$$K=K_0+C_K/(T-\Theta_K). \tag{1}$$

The values for the parameters obtained from least-squares fit are given in Table II. The solid curves in Fig. 6 represent the calculated shift according to Eq. (1) with the proper values of the parameters.

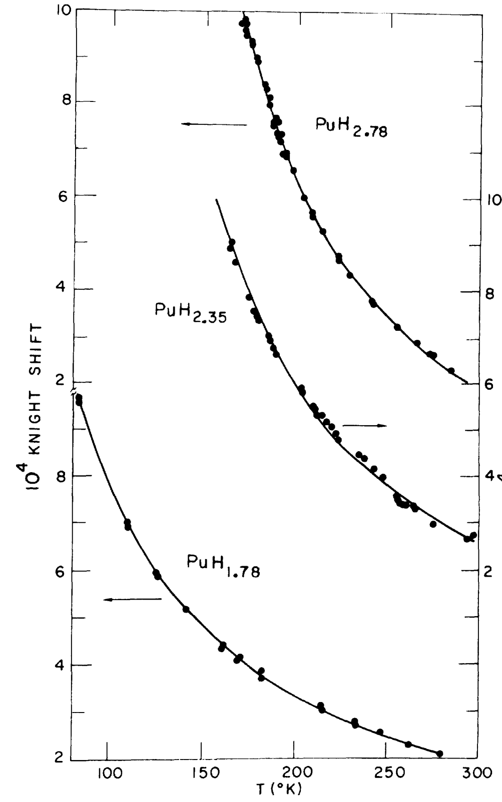

FIG. 6. Knight shift versus temperature for tetrahedral lines. The solid curves were obtained by least-squares fit to Eq. (1).

The shift results exhibit three important features: (i) An extended Curie-Weiss temperature dependence of K, for all samples, which means that all these hydrides are paramagnetic and may have an ordered magnetic phase at lower temperatures. This is clearly the case for $PuH_{2.78}$, which seems to become ferromagnetic at ~85 K, as can be seen from the absorption spectra in Fig. 4. (ii) C_k (of the tetrahedral protons) is nearly x independent. (iii) The shift of the octahedral protons is negligible, even at the lowest temperature.

TABLE II. Knight-shift parameters for the tetrahedral lines.

x(H/Pu)	1.78	2.35	2.65	2.78
$10^{+4}K_0$	-0.8 ± 0.1	-1.8 ± 0.2	-2.7 ± 0.2	-3.2 ± 0.3
$C_K(10^{-2}$ K)	8.2 ± 0.2	10.2 ± 0.6	10[a]	11.0 ± 0.7
Θ_K(° K)	5.0 ± 1.5	69.3 ± 3.7	63[b]	85.0 ± 3.5

[a] Assumed value.

[b] Calculated using Eq. (1) and the assumed value of C_K.

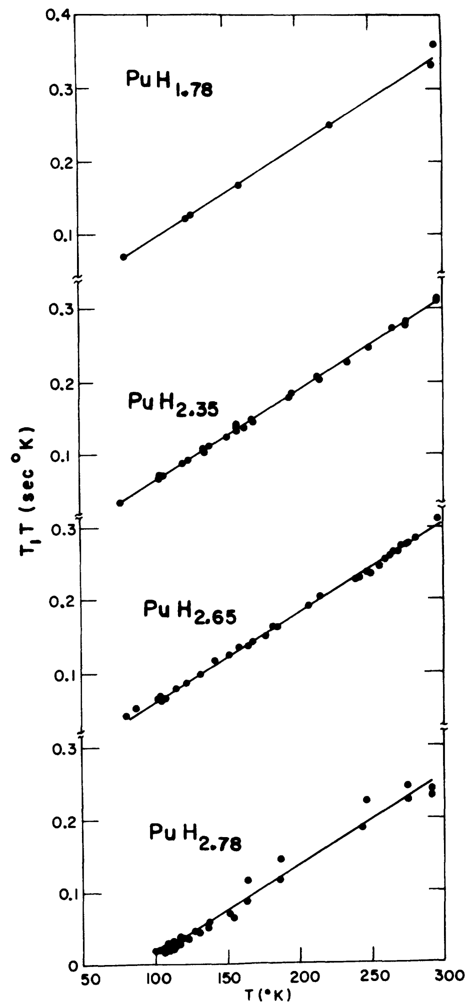

FIG. 7. T_1T vs T in plutoium hydrides. The solid curves were obtained by least-squares fit to Eq. (2).

C. Spin-lattice relaxation times

Spin-lattice relaxation times (T_1) of the different samples were measured from room temperature to 77 K at a frequency of 23 MHz. T_1 of $\mathrm{PuH}_{1.78}$ was also measured at 13 MHz, and no field dependence was observed. T_1 of each of the two lines of $\mathrm{PuH}_{2.65}$ was measured at 83 K and found to have the same value (540± 25 μsec), which means that both lines belong to protons of the same crystallographic phase. A similar behavior is found in $\mathrm{PuH}_{2.78}$. The room-temperature values of T_1 are nearly equal for all samples. These values are much shorter than those found in the nonparamagnetic thorium and lanthanum hydrides. The typical metallic temperature dependence of T_1, namely, $T_1T=\text{const}$, was not observed in the plutonium hydride system. A least-squares fit of the experimental results to the form $T_1T=C_R(T-\Theta_R)^\gamma$ was carried out for the different compositions. The values $\gamma=1.15\pm0.15$, 1.026 ± 0.03, 1.11 ± 0.15, and 0.9 ± 0.1 for $x=1.78$, 2.35, 2.65, and 2.78, respectively, were obtained. Therefore, we assume that $\gamma=1$ for all compositions. The solid curves in Fig. 7 represent the least-squares fit of the results to a form

$$T_1T=C_R(T-\Theta_R). \tag{2}$$

The values of the parameters C_R and Θ_R, so obtained, are given in Table III.

IV. DISCUSSION

In rare-earth paramagnetic intermetallic compounds, the nuclear moment I_i on the nonmagnetic site was found[15] to be coupled to the spin component S_k of the total magnetic moment μ. This coupling is of the exchange type $\vec{I}_i\cdot\vec{S}_k$. On quite general grounds it can be shown that the shift is given by

$$K=K_0+H_{\mathrm{eff}}\langle\langle S_z\rangle\rangle/H\,, \tag{3}$$

where H_{eff} is an effective field per Bohr magneton at the nonmagnetic nucleus, and $\langle\langle S_z\rangle\rangle$ is the thermal average spin of the magnetic moment. If the $5f$ configuration of the plutonium atoms can be described by a single J, then, using the operator equivalence $S_z=(g_J-1)J_z$, one obtains

$$\langle\langle S_z\rangle\rangle/H=(g_J-1)(\chi_f/Ng_J\mu_B)\,. \tag{4}$$

Here N is Avogadro's number, g_J is the Landé g factor, and χ_f is the susceptibility of the $5f$ electronic moment. In this case, K will be linear in χ_f. When J mixing is important, as was found to be the case in many actinide compounds, the ratio K/χ may be a strong function of temperature, and a full mixed-J calculation of $\langle\langle S_z\rangle\rangle$ and $\langle\langle \mu_z\rangle\rangle$ must be made.[16]

Two models of the $\vec{I}\cdot\vec{S}$ interaction have been generally employed. The first model involves the indirect hyperfine interaction, sometimes referred to as the RKKY interaction. In this

TABLE III. Spin-lattice relaxation parameters.

x	1.78	2.35	2.65	2.78
C_R (msec)	1.28 ±0.04	1.25 ±0.01	1.24 ±0.01	1.24 ±0.05
θ_R(°K)	26.0 ±6.0	49.0 ±1.0	50.5 ±1.5	86.0 ±4.0

model, the spin of the localized moment polarizes the conduction electrons via an effective exchange interactions $J_{\sigma f}\vec{\sigma}\cdot\vec{S}$. Here $J_{\sigma f}$ are the effective σ–f exchange constants, and σ signifies the s, p, and d conduction-electron spins. The polarized conduction electrons then interact with the nuclear spins via the contact, or core-polarization, hyperfine interactions. In our case, the NMR nucleus is a proton, and only s-type conduction electrons contribute to the hyperfine interaction. This is also correct to a very good approximation for P and Al nuclei, where the p-type conduction-electron contribution is negligible. In this model, according to Fradin,[4] H_{eff} and T_1 are given for weak crystal fields by

$$H_{\text{eff}} = J_{sf} N_s(E_F) H_{\text{hfs}} \tag{5}$$

$$T_1^{-1} = T_{1K}^{-1}\left(1 + 4N_s(E_F)(g_J - 1)^2 \frac{J(J+1)\,|J_{sf}(q)|^2}{3k_B[T - \Theta(q)]}\right). \tag{6}$$

Here T_{1K}^{-1} is the familar Korringa relaxation rate

$$T_{1K}^{-1} = [\pi\gamma_n^2 \hbar k_B H_{\text{hfs}} N_s^2(E_F)]\,T. \tag{7}$$

Here $J_{sf}(k)$ is the k Fourier component of the $s-f$ exchange integral, and $N_s(E_F)$ is the density of s-type conduction-electron states, for one spin direction, at the Fermi level. Fradin assumed for his derivations that the excitation processes at the Fermi surface are dominated by a critical wave vector, i.e., that $\chi^{\pm}(q = Q)$ dominate the fluctuations in the susceptibility. As is known

$$\theta(q) = \lambda(q)(g_J - 1)^2 J(J+1)/3k_B ,$$

where $\lambda(q)$ is the wave-vector-dependent constant of the molecular field. For ferromagnets $\Theta_R = \Theta_K$ (because $Q = 0$), as was found in $PuH_{2.78}$. As long as the crystal-field mixing is negligible, the magnetic susceptibility can be given by

$$\chi = N g_J J(J+1)\mu_B^2/3k_B(T - \Theta_K) ,$$

and, for the ferromagnetic case, it can be substituted into Eq. (6). Combining Eqs. (3), (4), and (6) and using the notations $\alpha = dK/d\chi$ and $\beta = d(T_1 T)^{-1}/dK$, one obtains

$$\beta = 4\pi\gamma_n^2 h k_B N_s(E_F) N\alpha \tag{8}$$

from which the density of s states can be calculated. For $PuH_{2.78}$ we find $\beta = 1/C_R C_K \simeq 7330$. The value of α cannot be calculated directly because we do not have susceptibility measurements for this system. Hence, we shall use the shift of the ferromagnetic NMR line to calculate α. The internal field at the proton site is given by $H_{\text{int}} = N \bar{n}_f \mu_B \alpha$, where $\bar{n}_f$ is the thermal average of the saturation moment, in μ_B units. According to Ref. 7, $\bar{n}_f = 0.24$ at 77 K, when the sample is cooled down in the presence of a 600 G field. The value of $\bar{n}_f$ can be affected by the strength of this field because of the large coercive forces expected in actinide systems. We cooled the sample in a higher field and therefore assume $\bar{n}_f = 0.27$, hence $\alpha = 2.9$ emu/mole. From Eq. (8) we derive $N_s(E_F) = 5.2$ states/eV spin, which is too high for the S conduction band. This could result from the neglect of an appreciable J mixing due to strong crystal-field interactions, which can greatly change the relations between χ, K, and T_1. These quantities were also calculated[16] for the strong crystal-field case, but the symmetry of our nonstoichiometric system is too complicated to actually calculate the lowest-energy crystal-field states. For a rough estimation, we can derive H_{eff} from Eqs. (3) and (4) as, assuming a P_u^{3+} ionization state ($5f^5$ configuration with $g_J = \frac{2}{7}$), $H_{\text{eff}} = -6.5$ kOe. Unfortunately, we cannot deduce it directly from T_{1K} because the relaxation rate is dominated mainly by the second term in Eq. (6). If we assume the same value for H_{hfs} in PuH_x as was found[8] for β-UH_3, namely $H_{\text{hfs}} = 19.6$ kOe, we obtain $J_{sf} = -6.4\times 10^{-2}$ eV.

The second model of the $I-S$ interaction assumes a transfered hyperfine interaction (thf) between the nucleus of the nonmagnetic ion and the paramagnetic moments. In this model, the ligand and the metal-ion wave functions are admixed in the molecular orbital, thereby transferring a fraction of unpaired spin of s character f_s, to the ligand orbit per actinide ion nearest neighbor. Here H_{eff} is given by[17]

$$H_{\text{eff}} = M H_{\text{hfs}} f_s/2S , \tag{8}$$

where M metal ions surround each anion, and $2S$ is the number of unpaired $5f$-electron spins. For tetrahedral protons, $M = 4$, and, for octahedral protons, $M = 6$. Under the above assumptions $f_s(H_t) = 0.4$ and $f_s(H_0) = 0.28$. In this model, a similar temperature dependence for the spin-lattice relaxation time $T_{1\,\text{thf}}$ was derived by Grunzweig-Genossar and Fibich[18] under certain approximations and a spin diffusion form for the spin correlations.

The thf model was used[19] to explain the composition independence of $\alpha = \partial K/\partial\chi$ in the $UP_{1-x}s_x$ system. Moreover, all spin-lattice relaxation results[20] of this system seem to have a temperature dependence of the form of Eq. (2), with a composition-independent value for C_R. On the other hand, the strong composition dependence of the U – U magnetic coupling was assumed to result from an RKKY mechanism.[21] Hence, it was assumed that the RKKY mechanism is not effective in the U – P coupling because of the negative screening of the phosphor P^{3-} nucleus. Such a screening is, however, less effective for protons. Despite the fact that the thf relaxation mechanism does not depend on the presence of conduction electrons, a temperature dependence of the form of Eq. (2) has only been found in metallic actinide compounds and in rare-earth dialuminide.

If the conduction electrons do not play an important role in the line shift and spin-lattice relaxation, one expects some composition dependence of C_K and C_R, as can be seen from Eqs. (3), (5), and (6), unless a broad s band and a narrow d band exist at the Fermi level. The s band may account for the Pu-proton coupling, whereas the Pu-Pu magnetic coupling may be mainly via the d-type conduction electrons as a result of a d-f exchange interaction. $N_d(E_F)$ may vary appreciably with x, whereas $N_s(E_F)$ and the associated NMR properties of the nonactinide nucleus would not. Moreover, the composition dependence of the Fermi wave vector k_F of these bands may be quite different, and no simple comparison can be made between the actinide-actinide coupling and the actinide-protons coupling.

It is worth mentioning here that the application of a rigid-band model for metallic hydrides is not justified for some cases.[22] The octahedral protons may form new states below the valence band and have no effect on the s band at the Fermi surface. Such a model is consistent with the x-ray emission study[23] of the isostructural LaH_x system, which indicates the existence of partial covalency (about equal to that of lanthanum oxide) for the trihydride. Such a model may explain the composition independence of C_K and C_R and the big difference in the line shifts of the two types of protons. Furthermore, the negligible Knight shift and inhomogeneous broadening of the octahedral protons may result from an associated change in the valence of nearest-neighbor plutonium ions from Pu^{3+} to Pu^{2+}, which are nonmagnetic. The results of a recent Mössbauer study[24] on the NpH_x system may be interpreted by assuming similar variations in the local moments. Such variations may be checked by magnetization measurements as long as the crystal-field effect is not too strong, or by neutron diffraction.

V. SUMMARY OF RESULTS

(i) The proton spectra are composed of two lines with different areas, linewidths, and shifts. From the ratio of the integrated intensities, each line seems to belong to protons in different crystallographic sites, H_{tet} and H_{oct}.

(ii) The shift of H_{tet} is of the form $K = K_0 + C_K/(T - \Theta_K)$, where C_K is nearly composition independent. The Knight shift of H_{oct} is zero within experimental error.

(iii) The values and composition dependence of the hydrogen diffusion constants were found to be quite similar to those in the lanthanum hydride system. This indicates that a similar diffusion mechansim exists in both systems. A different diffusion rate was found for the different kinds of hydrogen ions, where the jump rate $\nu(H_{\mathrm{oct}}) > \nu(H_{\mathrm{tet}})$.

(iv) The spin-lattice relaxation times have a temperature dependence of the form $T_1 T = C_R(T - \Theta_R)$, which indicates that the Pu ions have localized magnetic moments. C_R was found to be composition independent.

(v) Θ_R and Θ_K increase strongly with hydrogen concentration. This indicates a probable increase in the magnetic transition temperature with x and is in contrast to the situation in the isostructural rare-earth hydrides.

(vi) The strong dependence of Θ_K on the hydrogen concentration, which is in contrast to weak dependence of C_K and C_R, seems to indicate that the localized magnetic moments are coupled mainly via the d-type conduction electrons.

(vii) An NMR absorption line of $\mathrm{PuH}_{2.78}$ was observed in the ferromagnetic phase down to 77 K.

(viii) At low hydrogen concentrations $\Theta_R \neq \Theta_K$. This is characteristic to antiferromagnetic phase transition.

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