conf. 790301--8

MASTER

IS-M--178

Hydrogen Diffusion and Electronic Structure Parameters In Tantalum Hydrides Determined by Pulsed NMR Measurements

P. A. Hornung,* A. D. Khan,† D. R. Torgeson, and R. G. Barnes
Ames Laboratory-USDOE and Departments of Physics
and Materials Sciences, Iowa State University, Ames, Iowa 50011

ABSTRACT

Measurements are reported of the proton spin-lattice relaxation time T_1 in the tantalum-hydrogen system over the temperature and composition ranges, $77\ K \leq T \leq 470\ K$ and $0.155 \leq H/Ta \leq 0.677$, respectively. In the high temperature, solid-solution (α) phase, the activation energy for hydrogen diffusion determined from the dipolar contribution to T_1, shows a weakly increasing trend from 0.134 eV/atom at H/Ta = 0.155 to 0.140 eV/atom at H/Ta = 0.677. Boundaries between ordered hydride phases and the α phase, located by the occurrence of abrupt changes in T_1, agree very well with other recent determinations. The quantity $(T_{1e}T)^{-1/2}$, based on the conduction electron contribution, $(T_{1e})^{-1}$, to the relaxation rate $(T_1)^{-1}$, is proportional to the density of states at the Fermi level $N(E_F)$. $(T_{1e}T)^{-1/2}$ decreases linearly with increasing hydrogen concentration, similarly to its behavior in the V-H and Nb-H systems.

INTRODUCTION

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Although the Group VB metal-hydrogen systems have been the subject of much intense recent study by a variety of methods, the structural, diffusive, and electronic nature of these hydrides retain many unresolved features. Fig. 1 presents a recent compilation of phase information for the tantalum-hydrogen system based on DTA and susceptibility measurements.[1,2] The essential features of this phase diagram are that at high temperatures (i.e., $T \gtrsim 360$ K) hydrogen exists in solid solution in the body-centered cubic structure of Ta metal, the lattice parameter being very slightly expanded at high hydrogen concentrations. At lower temperatures, ordering of the hydrogen occurs on some subset of the available interstitial sites, leading to a variety of ordered hydride phases (at least 5) and accompanying two-phase regions. Although structural features of some of these phases are known, little is known of their electronic properties and of hydrogen diffusion within them.

Previous NMR investigations have provided a variety of information about the Group VB hydrides. For example, Lütgemeier, et al.[3] in the case of niobium hydrides and Pedersen, et al.[4] in the case of the tantalum hydrides showed that diffusion was the primary relaxation mechanism for proton spins over a fairly wide temperature range about room temperature.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

8

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Furthermore, these references indicated that the high temperature transition to the α phase caused the appearance of a discontinuity in the value of T_1. Pedersen, et al.[4] also noted some further effects in the Ta-H system. Composition and temperature regions existed in which recovery of the nuclear magnetization was characterized by a non-single exponential decay. These indications were not pursued further, however.

In this report we describe measurements of the proton spin-lattice relaxation time T_1 in tantalum hydrides. These measurements yield information concerning the electronic density of states and the activation energy for diffusion in the solid solution (α) phase. In addition, by utilizing an improved pulsed radio frequency spectrometer system, we have been able to observe unambiuously the occurrence of two-phase regions in the phase diagram by means of the appearance of two-exponential decays of the nuclear magnetization signal.

EXPERIMENTAL ASPECTS

All data were taken at a nominal frequency of 40.0 MHz using a 30 cm electromagnet with a 7.6 cm gap at a field strength of 9.395 kOe. The pulsed radio frequency spectrometer has as its source a frequency synthesizer which also provides the 10 MHz time base signal for the pulse programmer. As a result, both the starting edges of the logic pulses and the rf pulses themselves are phase coherent. The programmer is of the Conway and Cotts design[5] with additional circuitry[6] to automatically increment the pulse spacing τ when performing the "180° - τ - 90° - free induction decay (FID)" sequence. The final pulsed rf stage delivered about 800 watts of power into the transmit-sample probe-receive network which was the matched transmission line system of Lowe and Tarr.[7] To insure high voltage insulation and provide external tuning capability, a probe composed of concentric brass cylinders insulated by 430 μm teflon was used in a design following Gottlieb, et al.[8] The free induction decay (FID) signals were amplified by a special limiting amplifier with less than one microsecond recovery time to full gain as described previously,[9] then phase-sensitively detected, amplified, and filtered by a wide-band video amplifier,[10] digitized and stored with in a Nicolet Instruments 1072 signal averager.

The spin-lattice relaxation times were determined by the inversion-recovery method which monitors the amplitude of a point on the FID signal after the initial inversion of the nuclear magnetization by the 180° rf pulse. The sequence used was 180° - τ - 90° - FID - wait $6T_1$ - repeat with incremented τ. The amplitude at a fixed point in time after the 90° pulse was measured and stored in one channel of the signal averager. The signal amplitudes for successively incremented values of τ were stored in successive channels of the averager. By repeating the entire range of τ increments the signal/noise quality of the magnetization recovery curve was enhanced. Accurate measurement of the τ-increment and determination of the baseline value (amplitude at infinite time) of the magnetization furnish the additional information needed to derive T_1 from the stored record of magnetization recovery. The latter was accomplished by interfacing the signal averager to a DEC PDP-15 computer which computed a weighted least-squares fit to an exponential (or sum of two exponentials) and provided a measure of the quality-of-fit. An example of such a two-exponential fit is shown in Fig. 2 to illustrate the typical character of the magnetization recovery behavior in a two-phase region.

Enclosed by layers of insulation, the probe assembly was electrically heated to 500 K or alternatively cooled to 100 K through variable heat-leak rods to a liquid nitrogen reservoir. Temperatures were measured and regulated using a pair of copper-constant thermocouples and a current controlled heater near the sample. Over a typical data acquisition period of two hours or less, the temperature was controlled to within 0.5 K, and in the worst cases, a 3 K temperature gradient was measured across the sample. Immersion of the entire probe in baths of liquid nitrogen and liquid oxygen was used to measure T_1 at 77.4 K and 90.1, respectively.

The Ta-H samples were prepared from the purest Ames Laboratory tantalum, with special precautions taken to avoid nitrogen and oxygen contamination. Hydrogen contents were determined by high temperature vacuum extraction. Representative results of this study are shown in Figs. 3 and 4 for samples with H/Ta ratios of 0.486 and 0.660.

α and α' PHASES

In a metallic hydride, one expects two predominant sources of proton spin-lattice relaxation: one is the electronic contribution due to the scalar contact interaction between spins of conduction electrons and protons, characterized by a relaxation rate $(T_{1e})^{-1}$; the other results from the modulation of the proton-proton dipolar interaction by the diffusive motion of the hydrogen and is characterized by the rate $(T_{1d})^{-1}$. In general,

$$(T_1)^{-1} = (T_{1e})^{-1} + (T_{1d})^{-1} \tag{1}$$

where T_1 is the measured, total spin-lattice relaxation time. The temperature dependence of the electronic contribution is characterized by the Korringa relation, $T_{1e}T$ = constant,[11] where the quantity $(T_{1e}T)^{-1/2}$ is proportional to the density of states at the Fermi surface. The diffusion dominated contribution $(T_{1d})^{-1}$ depends on the jump frequency ν_j for hydrogen motion in the lattice. $(T_{1d})^{-1}$ has its maximum value when ν_j approximately equals the Larmor frequency. In general, ν_j follows an Arrhenius relation of the form

$$\nu_j = \nu_o \exp(-E_a/kT) \quad , \tag{2}$$

where ν_o is a characteristic lattice vibration frequency and E_a is an activation energy, so that at temperatures either substantially higher or lower than that at which $(T_{1d})^{-1}_{max}$ occurs, one has $\ln T_{1d} \sim -E_a/kT$ (at high temperatures) or $\ln T_{1d} \sim E_a/kT$ (low temperatures).

In the solid solution α and α' phases at moderately high temperatures, the measured relaxation rates result from the combination of these two mechanisms which are comparable in strength. Since the relaxation rates $(T_{1e})^{-1}$ and $(T_{1d})^{-1}$ have known temperature dependences, a computer-assisted fit to the experimental data was made. This fit determines three parameters of interest: the activation energy for diffusion, the prefactor C in the $(T_{1d})^{-1} = C \exp(-E_a/kT)$ expression, and the $T_{1e}T$ product.

The results of this procedure are listed in Table I, where the listed uncertainties include an allowance for the fact that the data do not always include a sufficiently wide temperature range to insure that one of the two contributions dominated at one of the limiting temperatures.

Table I. Diffusion and electronic parameters obtained from analysis of the α and α' phase measurements of T_1.

Sample H/Ta	$T_{1e}T$ constant (sec-K)	Activation Energy (eV/atom)	Prefactor Rate C (10^{-2} $\sec^{-1}$)
0.155	116 ± 4	0.134 ± 0.010	0.8 ± 0.1
0.322	226 ± 15	0.133 ± 0.010	1.94 ± 0.10
0.486	330 ± 12	0.136 ± 0.010	2.40 ± 0.10
0.597	170 ± 10	0.144 ± 0.010	1.92 ± 0.18
0.660	2600 ± 100	0.142 ± 0.010	3.01 ± 0.20
0.677	1560 ± 300	0.143 ± 0.010	3.42 ± 0.20

Some very interesting conclusions can be drawn from this information. Despite some scatter in the results, the table gives a convincing presentation of the trends. First, the electronic contribution increases rapidly with increasing concentration. At the same time there occurs a gradual increase in the activation energy for hydrogen diffusion as well as an increase in the prefactor C.

The quantity $(T_{1e}T)^{-1/2}$ is proportional to the density-of-states at the Fermi level, $N(E_F)$, and is therefore expected to be proportional to the magnetic susceptibility χ. From Table I, this quantity decreases fairly linearly from 0.093 $(\sec K)^{-1/2}$ at H/Ta = 0.155 to perhaps 0.025 $(\sec K)^{-1/2}$ at H/Ta = 0.677. At the lower concentration, this value is very similar to that found in the Nb-H system, but at the higher concentration it is about half that in Nb-H. Susceptibility measurements on Ta-H samples by Ducastelle, et al.[12] and more recently by Köbler and Schober[1] show a decrease of about 20 to 25 percent in χ over the corresponding range of hydrogen concentration. It therefore appears that proportionality between $(T_{1e}T)^{-1/2}$ and χ changes with hydrogen concentration, with relaxation becoming less effective at the higher concentrations.

Assuming that for protons the interaction with the conduction electrons is dominated by the direct Fermi contact interaction, one has[13]

$$(T_{1e}T)^{-1/2} = \gamma_N \, (2hk)^{1/2} \, \rho H_{hf}^{(s)} \, N(E_F) \qquad (3)$$

where γ_N is the proton gyromagnetic ratio, h and k are Planck's and Boltzmann's constants, respectively, $H_{hf}^{(s)}$ is the effective hyperfine field for the direct Fermi contact interaction, and ρ is the fractional s character of the conduction band at the Fermi surface, i.e., $\rho = N_s(E_F)/N(E_F)$. Since χ reflects the behavior of $N(E_F)$, we conclude from the more rapid decrease of $(T_{1e}T)^{-1/2}$ that the s electron density-of-states $N_s(E_F)$ decreases with increasing hydrogen concentration in the Ta-H system.

The measured activation energies for hydrogen diffusion in the α phase are in good agreement with other recent determinations based on NMR and Mössbauer effect measurements. On the basis of the motional narrowing of the proton resonance, Tanaka and Hashimoto[14] determined that E_a = 0.144 eV for H/Ta = 0.10. Similarly, by studing the narrowing of the ^{181}Ta Mössbauer line, Heidemann, et al.[15] also concluded that E_a = 0.14 ± 0.01 eV for H/Ta = 0.15. The measurements reported here (Table I) indicate that no substantial increase in E_a occurs as the hydrogen concentration is increased to the α' phase.

STRUCTURAL INFORMATION

Structural information from these spin-lattice relaxation time measurements falls into three categories: the depth of the T_1 minimum, discontinuities in the slope of ln T_1 as a function of temperature or inverse temperature, and temperature regions in which two-exponential recovery of the magnetization is observed. In contrast to the α phase, the lower temperature ordered phases have hydrogen occupation restricted to subsets of the available interstitial sites, so that it appears probable that the diffusion process itself may be quite different within these several phases. This difference can be expected to appear as a discontinuity in the slope of ln T_1 when an ordered phase to α phase boundary is crossed and as two-exponential character of the magnetization recovery whenever the α phase and an ordered phase co-exist. The depth of the T_1 minimum, or alternatively the maximum relaxation rate, depends on the strength of the hydrogen-hydrogen and hydrogen-tantalum nuclear dipolar interactions. These depend in turn on known nuclear spin constants and lattice sums on r^{-6}, where r is the distance between two atoms. In principle, these interactions can provide a check on the ordered structures which have been proposed. However, the strong nuclear electric quadrupole interaction of ^{181}Ta induces a significant perturbation of its Zeeman levels so that its resonance condition is spread over such a wide range of frequencies (i.e., many MHz) that is contribution to the proton relaxation process becomes extremely difficult to assess. This situation is evidenced by the fact that despite our diligent efforts, observation of the ^{181}Ta resonance by wide-line (steady-state) methods has not been achieved, even in the cubic phase. The problem becomes more severe in the non-cubic phases, where we can estimate, on the basis of measurements made on ^{93}Nb in similar phases in the Nb-H and Nb-D systems,[16] that the quadrupole coupling constant for ^{181}Ta must be on the order of 50 to 100 MHz.

In essentially all of the known phase transitions that were traversed in these measurements, a two-exponential recovery region was evident in the data. Fig. 2 shows such an example for the two-phase $\beta + \alpha'$ region in the case of H/Ta = 0.597. For a combination of temperature and composition such that the relaxation times of the two components do not differ greatly, or if one component comprises less than about 10 percent of the volume of the sample, then this two-exponential decay characteristic is difficult to recognize and to analyze.

All of the phase transitions detected in this work are listed in Table II and are also shown in Fig. 1. Since the samples were powders and therefore subject to some inhomogeneity in hydrogen concentration (in comparison to single-crystal studies, for example), a differential thermal analysis (DTA) instrument (Dupont Model 900) was used to verify the phase transitions on these samples. Our DTA measurements showed excellent agreement with the NMR results and together they demonstrate conclusively that the regions of anomalous T_1 behavior are indeed associated with structural phase transitions.

Table II. Structural phase transitions and two-phase regions in the Ta-H phase diagram.

H/Ta	NMR Transition Temperatures (°C)	DTA Transition Temperatures (a) (°C)	Köbler & Schober Identification (b)
0.155	-60 to 23	very broad indication	α + β to α + ε to α
0.322	-73 to -13 (c)		α + β to α + ε
	5 to 45	35 ± 13	α + ε
	45 to 55		α + ε to α
0.486	34 ± 2	34 ± 1	β to ε
	60 ± 4 (d)	58 ± 1	ε to α
0.597	-60 to -10 (c)		θ to β + θ to β + δ
	45 to 51 (d)	41.0 ± 1.0	β + δ to β
		43.5 ± 1.0	β to α' + β to α' + ε to α'
0.660	45 to 61 (d)	47 ± 1	β + δ to α' + δ
		49.5 ± 1.0	α' + β to α'
0.677	-93 to -63		ξ + θ to θ to θ + δ
	-23 ± 10		θ + δ to β + δ
	45 to 63 (d)	58 ± 1	δ to α' + δ to α'

(a) No DTA measurements were made below 22°C.

(b) Ref. 1 in text.

(c) Two-exponential behavior was clearly observed throughout this two-phase region.

(d) Two-exponential behavior was observed in the transition region.

CONCLUSIONS

Measurements have been made of the proton spin-lattice relaxation T_1 in the Ta-H system over the temperature and composition ranges $77\ \text{K} \leq T \leq 470\ \text{K}$ and $0.155 \leq \text{H/Ta} \leq 0.677$, respectively. In the solid solution (α and α') phases, the quantity $(T_{1e}T)^{-1/2}$, based on the conduction electron contribution $(T_{1e})^{-1}$ to the total relaxation rate $(T_1)^{-1}$, decreases approximately linearly with increasing hydrogen concentration. Comparison with the behavior of the magnetic susceptibility over the same concentration range indicates that the relative s character of the conduction band decreases with increasing hydrogen concentration. Also in the solid solution phases, the activation energy for hydrogen diffusion shows a weakly increasing trend from 0.134 eV/atom at H/Ta = 0.155 to 0.140 eV/atom at H/Ta = 0.677. By utilizing an improved pulsed radio frequency spectrometer system, it has been possible to observe unambiguously the occurrence of two-phase regions in the phase diagram by means of the appearance of two-exponential decays of the nuclear magnetization signal. In addition, the occurrence of phase transitions, particularly those between the solid solution phases and the ordered phases, was observed as a sharp discontinuity in the temperature dependence of T_1. The phase boundaries and two-phase regions detected by these measurements are in excellent agreement with the most recent phase diagram of the Ta-H system based on DTA and susceptibility data.[1]

ACKNOWLEDGMENTS

We are indebted to Dr. D. T. Peterson and Mr. A. Johnson for their determinations of the hydrogen content of the samples investigated. This work was supported by the U.S. Department of Energy Office of Basic Energy Sciences, Materials Science Division.

REFERENCES

* Present address: Southwest Research Institute, San Antonio, TX 78284.
† Present address: NASA Lewis Research Center, Cleveland, Ohio.

1. U. Köbler and T. Schober, J. Less-Common Metals 60, 101 (1978).
2. T. Schober and A. Carl, Script Met. 11, 397 (1977).
3. H. Lütgemeier, R. R. Arons, and H. G. Bohn, J. Magn. Res. 8, 74 (1972).
4. B. Pedersen, T. Krogdahl, and O. E. Stokkeland, J. Chem. Phys. 42, 74 (1965).
5. J. L. Conway and R. M. Cotts, Rev. Sci. Instr. 48, 656 (1977).
6. D. J. Adduci, P. A. Hornung, and D. R. Torgeson, Rev. Sci. Instr. 48, 661 (1977).
7. I. J. Lowe and C. E. Tarr, J. Phys. E 1, 320 (1968).
8. A. M. Gottlieb, V. C. Srivastava, and P. Heller, Rev. Sci. Instr. 43, 676 (1972).
9. D. J. Adduci, P. A. Hornung, and D. R. Torgeson, Rev. Sci. Instr. 47, 1503 (1976).
10. D. R. Torgeson and D. J. Adduci, unpublished work.
11. J. Korringa, Physica 16, 601 (1950).
12. F. Ducastelle, R. Caudron, and P. Costa, J. Phys. Chem. Solids 31, 1247 (1970).
13. Y. Yafet and V. Jaccarino, Phys. Rev. 133, A1630 (1964).
14. K. Tanaka and T. Hashimoto, J. Phys. Soc. Japan 34, 379 (1973).
15. A. Heidemann, G. Kaindl, D. Salomon, H. Wipf, and G. Wortmann, Phys. Rev. Letters 36, 213 (1976).

16. Y. S. Hwang, D. R. Torgeson, and R. G. Barnes, Solid State Commun. 24, 773 (1977).

FIGURE CAPTIONS

Fig. 1. Phase diagram of the Ta-H system according to Köbler and Schober.[1] Phase transitions detected by NMR measurements in this work are indicated by vertical bars.

Fig. 2. Example of two-exponential behavior in the recovery of the longitudinal nuclear magnetization signal in a two-phase region ($\beta + \alpha'$) of the Ta-H system.

Fig. 3. Dependence of the proton spin-lattice relaxation time T_1 on inverse temperature in $TaH_{0.486}$. Phase boundaries are indicated according to Ref. 1.

Fig. 4. Dependence of the proton spin-lattice relaxation time T_1 on inverse temperature in $TaH_{0.660}$. Phase boundaries are indicated according to Ref. 1.

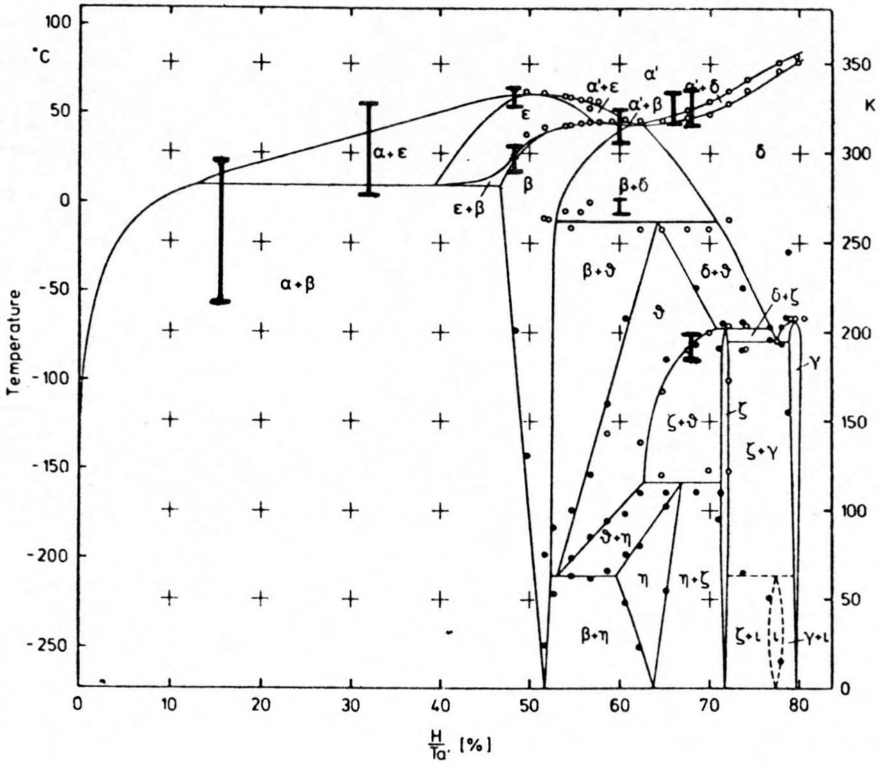

Figure 1. Phase diagram of the Ta-H system according to Köbler and Schober.[1] Phase transitions detected by NMR measurements in this work are indicated by vertical bars.

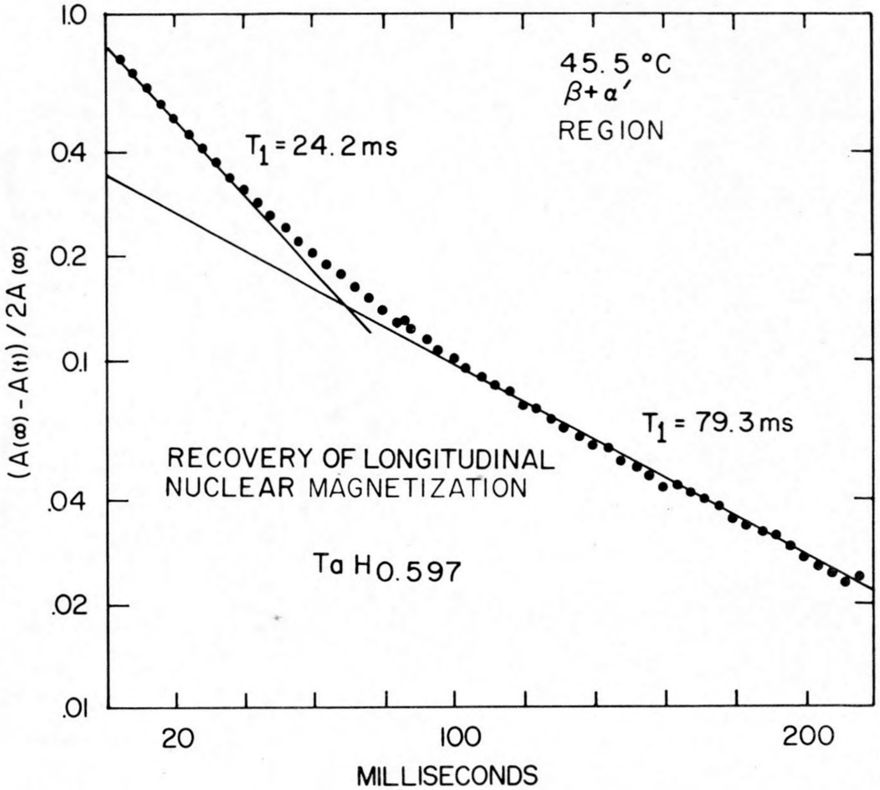

Figure 2. Example of two-exponential behavior in the recovery of the longitudinal nuclear magnetization signal in a two-phase region (β + α') of the Ta-H system.

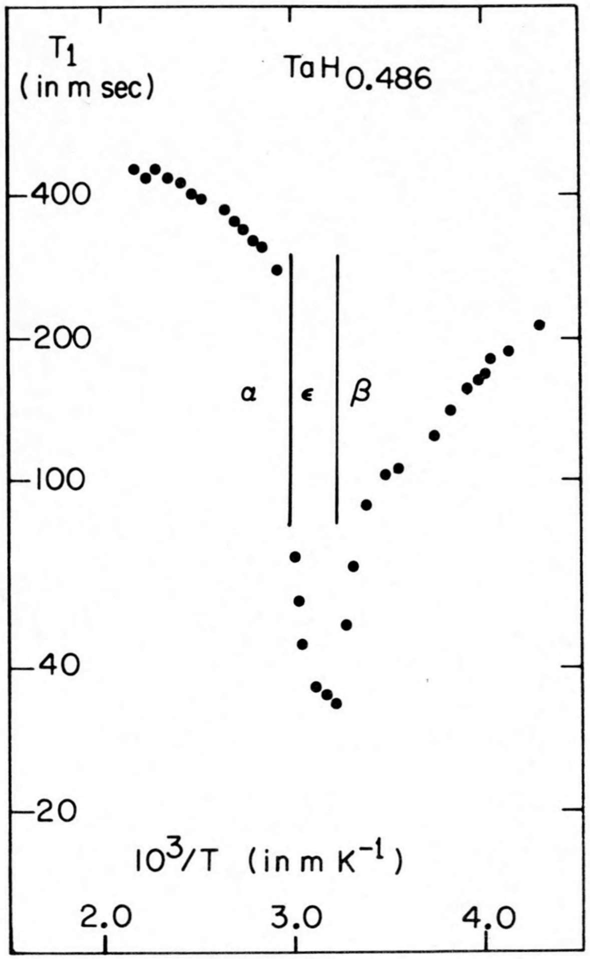

Figure 3. Dependence of the proton spin-lattice relaxation time T_1 on inverse temperature in $TaH_{0.486}$. Phase boundaries are indicated according to Ref. 1.

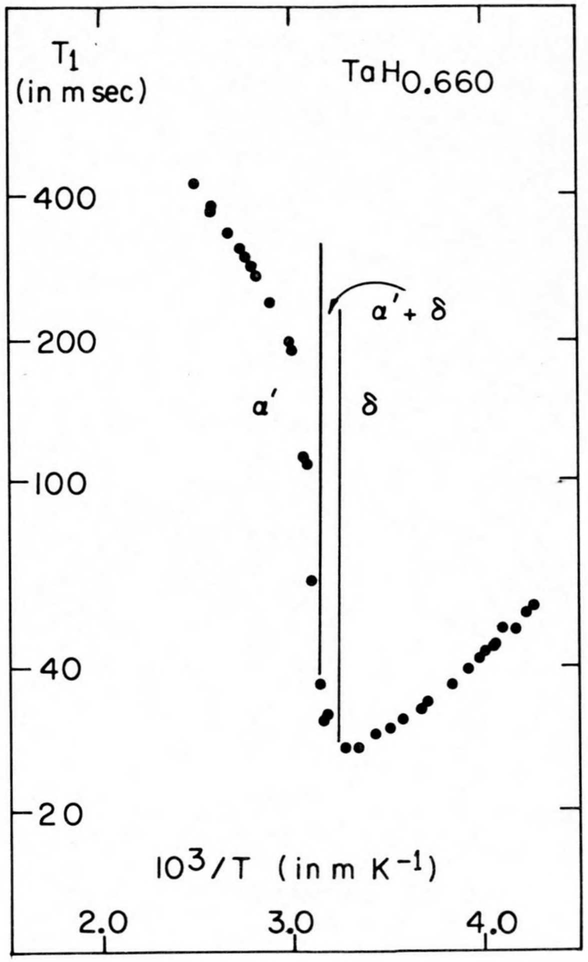

Figure 4. Dependence of the proton spin-lattice relaxation time T_1 on inverse temperature in $TaH_{0.660}$. Phase boundaries are indicated according to Ref. 1.