

Nuclear-Acoustic-Resonance Study of the Diffusion of Hydrogen and Deuterium in Tantalum

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The ^{181}Ta relaxation rate is determined by nuclear acoustic resonance in TaH_x and TaD_x ($0.0003 \leq x \leq 0.0324$) for temperatures between 100 and 370 K. The nearest-neighbor quadrupolar interaction with the diffusing H or D which is responsible for the relaxation amounts to $e^2qQ/\hbar = 5.4 \times 10^9$ and $4.7 \times 10^9 \text{ s}^{-1}$, respectively, i.e., it exceeds by far the Zeeman interaction. The experimental results are discussed with respect to this rather unusual situation and compared with macroscopic diffusion experiments.

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Conventional nuclear magnetic resonance (NMR) has proved to be a very successful method in studying the diffusion of hydrogen in metals.¹ In all but one of the studies (the diffusion of surplus H in LaH_{2+x})² the mobile H or D nuclei themselves have been used as NMR probes, thereby restricting the experiments to substantial hydrogen concentrations. In the case of tantalum, however, the extremely high nuclear quadrupole moment ($Q \cong 4 \text{ b}$ for ^{181}Ta) favors the observation of the host nuclei by the technique of quadrupolar nuclear acoustic resonance (NAR), where the signal intensity is proportional to Q^2 .^{3,4} In addition, the high Q allows, by quadrupolar relaxation, the study of very small hydrogen concentrations and of their diffusion in the unperturbed α phase down to low temperatures.⁵⁻⁷ In the following the principal results of a comprehensive NAR study of TaH_x and TaD_x are presented. Apart from the diffusion properties, we will also discuss qualitatively the experimental consequences of a physical situation very unusual in relaxation theory, which arises from the high magnitude of the quadrupolar interaction in these two systems.

A number of commercial Ta single crystals were prepared as acoustic resonators,³ tempered at 2600°C and below 10^{-7} Pa , and charged electrolytically.⁷ The absorbed H or D concentrations were determined by a novel acoustic method,⁷ and later by outgassing. It is known from earlier experimental⁵ and theoretical⁸ work that the NAR linewidths in $\alpha\text{-TaH}_x$ are essentially determined by diffusing hydrogen atoms via quadrupolar relaxation. From the linewidths the transverse relaxation rates Γ_q were derived, using a theory of NAR line shapes by Fedders.⁹ To separate Γ_q in the case of narrow lines from other contributions (homogeneous or inhomogeneous) it was assumed that these contributions

were temperature independent. Although all data shown in this Letter were obtained from the quadrupolar NAR-2 (i.e., $\Delta m = 2$) linewidths, the like-

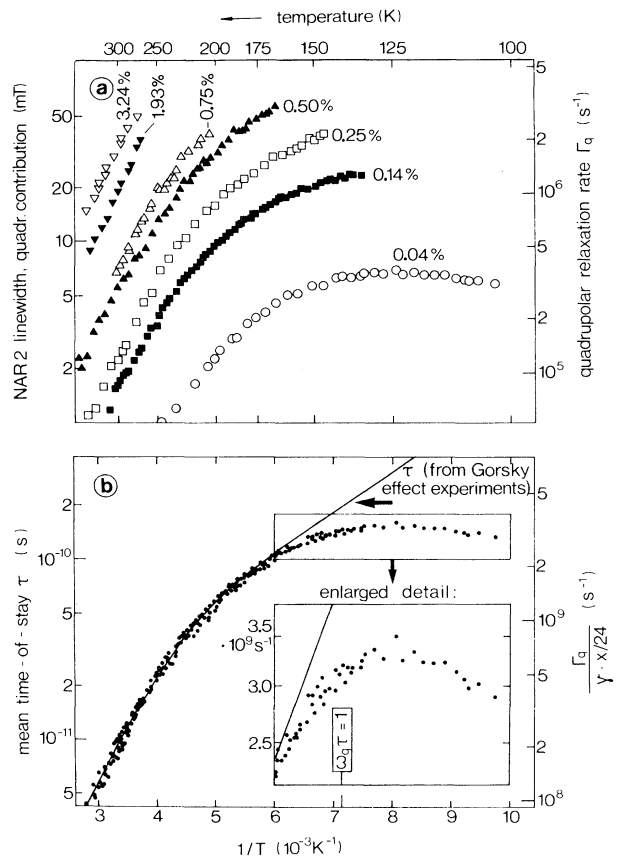


FIG. 1. (a) Arrhenius plot of the peak-to-peak NAR-2 linewidth (quadrupolar contribution from diffusing hydrogen only) of ^{181}Ta in TaH_x . (b) Quadrupolar relaxation rate Γ_q , reduced to the same concentration x [experimental points from (a), right-hand scale], superimposed with values for the mean time of stay, τ , obtained from Gorsky-effect experiments (Ref. 10) (full line, left-hand scale). The fit of τ to the data points yields $\omega_q = 5.4 \times 10^9 \text{ s}^{-1}$, with use of Eq. (1).

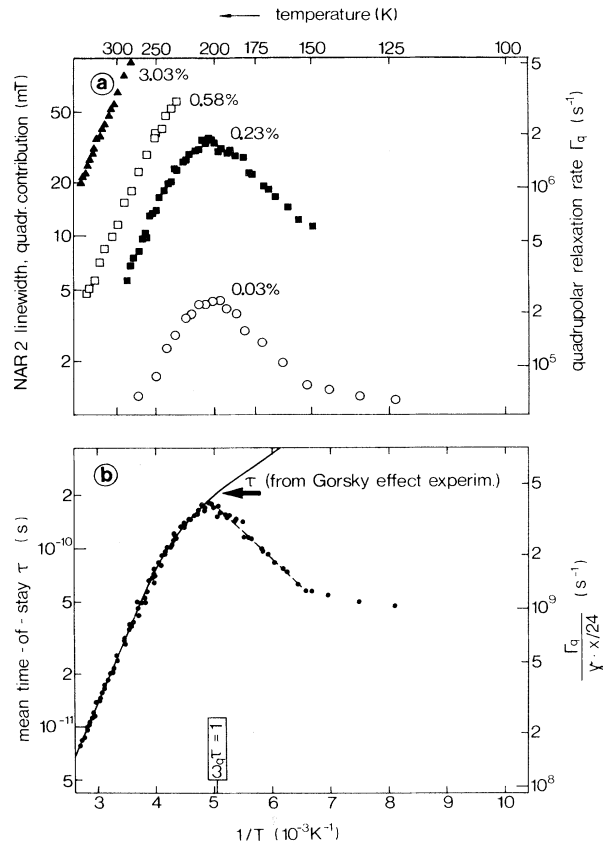


FIG. 2. (a) and (b) Experimental results for TaD_x in the same graphical representation as in Fig. 1. The high-temperature fit yields $\omega_q = 4.7 \times 10^9 \text{ s}^{-1}$. The dotted line corresponds to a low-temperature dependence as τ^{-1} with an activation energy of 60 meV.

wise recorded NAR-1 spectra are consistent with these results in all aspects. The experiments were performed with standard NAR equipment³ at ultrasonic frequencies near 20 MHz (corresponding to a Larmor frequency $\omega_0 \cong 6 \times 10^7 \text{ s}^{-1}$ for NAR-2).

Figures 1(a) and 2(a) show the experimental relaxation rates Γ_q as a function of the reciprocal temperature for seven samples of TaH_x and four samples of TaD_x , with x ranging over two decades from 0.03% to 3.24%. The main consequences of these results are listed below.

(1) The relaxation rates Γ_q are proportional to the concentration x throughout the experiment. This is clearly seen from the lower part (b) of the figures where, after division of the rates Γ_q by x , all the experimental data points coincide. Also it follows that, with the described sample-preparation technique, trapping effects⁶ are apparently of no importance even for concentrations

as low as 0.03%.

(2) In the high-temperature range, Γ_q is proportional to the mean time of stay, τ , obtained from macroscopic diffusion (Gorsky effect) experiments¹⁰; τ is shown as a full line in Figs. 1(b) and 2(b) (left-hand scale). This motional narrowing behavior follows also from the theoretical treatment by Fedders⁸ and Swendsen and Kehr,¹¹ who obtained, by a model calculation including only nearest-neighbor (nn) interaction,

$$\Gamma_q = (x/24)\gamma\tau\omega_q^2. \quad (1)$$

γ is a slightly anisotropic numerical factor of about 5 for NAR-2, and ω_q is the nn quadrupolar coupling constant, which is assumed in the calculation to be a small perturbation compared with the Zeeman splitting.

(3) In accordance with the macroscopic τ ¹ and with recent Mössbauer results,¹² we find a deviation from the high-temperature Arrhenius line towards lower activation energies for both H and D below about 250 K. The occurrence of a decrease in activation energy with decreasing temperature has been attributed to effects of thermally activated tunneling,¹³ or to pair diffusion.¹⁴ Our experiments show that the bend occurs at the same temperature for concentrations differing by more than one decade. This observation is in contradiction to the assumption of pair diffusion because it would imply a low-temperature contribution proportional to x^2 instead of x .

(4) By fitting the reduced relaxation rate values $\Gamma_q/(\gamma x/24)$ (right-hand scale) to the macroscopic τ , the following results are obtained from (1) for the nn quadrupolar interaction:

$$\begin{aligned} \omega_q &= 5.4 \times 10^9 \text{ s}^{-1} \text{ for H,} \\ \omega_q &= 4.7 \times 10^9 \text{ s}^{-1} \text{ for D.} \end{aligned} \quad (2)$$

These values are reasonable. Assuming a single-charged point defect with a screened Coulomb potential on a tetrahedral interstitial site, a screening length of 0.5 Å, and a Sternheimer factor of 60, one obtains $\omega_q = 4.5 \times 10^9 \text{ s}^{-1}$.

(5) Below 160 K for H and 210 K for D the Γ_q values begin to deviate from the proportionality to the macroscopic τ , and even show a decrease with further decreasing temperature. It should be mentioned that the NAR-2 spectra with a linewidth $\geq 10 \text{ mT}$ possess an excellent Lorentzian shape in the whole temperature range, indicating the predominance of a single rate Γ_q .

These findings shall now be interpreted on the basis of the known properties of hydrogen in Ta

metal.¹⁵ The H or D impurities are assumed to occupy tetrahedral interstitial sites in the bcc Ta lattice, and to move rapidly between these sites by uncorrelated, thermally activated jump diffusion. When staying at one site the charged defects produce an electric field gradient (EFG) at nearby Ta nuclei. In the high-temperature range the quadrupolar relaxation rate Γ_q of a given Ta nucleus is proportional to the correlation function of the fluctuating EFG seen by this nucleus.^{8,16} Because the contribution of different interstitial sites to the EFG correlation function drops as the sixth power of the distance even for an un-screened Coulomb potential, one can estimate that at least 90% of Γ_q is dominated by the interaction with the 24 nn tetrahedral interstitial sites of every Ta nucleus.⁷ Therefore we can use the simplified model,^{8,11} assuming that the quadrupolar interaction is "switched on" only as long as a nn interstitial site is occupied; otherwise, which is the case during most of the time for $x \ll 1$, the interaction is thought to be "switched off."

It is remarkable that the instantaneous magnitude ω_q of this interaction given in (2) exceeds the Zeeman interaction by nearly two orders of magnitude. Consequently a nucleus with a nn defect is characterized quantum mechanically by "quadrupole states" (with a small magnetic dipolar perturbation), and not by Zeeman states. These quadrupole states, however, are only defined for lifetimes longer than ω_q^{-1} , i.e., for $\omega_q \tau > 1$. With the τ values given in Figs. 1 and 2 this is the case below about 140 K for H and 200 K for D. In both cases these temperatures are close to the point where Γ_q begins to deviate from the behavior given by (1).

At high temperatures ($\omega_q \tau < 1$) the visit of a nuclear spin by a diffusing H or D on a nn site can be described in terms of a small "dephasing", which leads to the motional narrowing behavior $\Gamma_q \propto \omega_q^{-2} \tau$ of Eq. (1) (weak collision range).¹⁶ Still, it must be emphasized that the proportionality factor in Eq. (1) has been derived under the assumption of ω_q being a small perturbation,⁸ which is certainly not applicable in our case. In the low-temperature range ($\omega_q \tau > 1$) the nuclei contribute to the NAR signal only as long as they have no nn defect. (Otherwise, corresponding to a small fraction of $4x$ of the time, they occupy quadrupole states.) The NAR relaxation rate is now governed by the lifetime of the "unperturbed" state between two nn visits. It should therefore be proportional to x/τ and independent of ω_q

(strong collision range). Figure 2(b) for D indeed shows that the negative slope of Γ_q in this range corresponds to an activation energy of 60 meV, which is comparable with the Gorsky-effect value¹⁰ of 46 meV at the same temperature. In the case of H, Völkl and Alefeld¹⁰ state a low-temperature activation energy of 40 meV down to 90 K. Here the flatness of our curve below 150 K can be an indication that the activation energy is actually considerably lower.

In conclusion, we want to recapitulate that the described experiment is characterized by a huge magnitude of the quadrupolar interaction, which exceeds by far the Zeeman splitting, whereas usually for quadrupolar² (or dipolar) relaxation the opposite is the case. We feel that our experimental situation is unique in that sense, and that it deserves further theoretical consideration. Because the NAR technique allows a very precise linewidth determination, especially for a high- Q nucleus, a quantitative theoretical treatment of this relaxation case would provide a chance to study the diffusion of H and D in Ta single crystals even below 100 K. This would be of great interest for the presumed nonclassical diffusion behavior¹³ of hydrogen in tantalum.

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Magnetic Confinement of Spin-Polarized Atomic Hydrogen

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Magnetic confinement is used to obtain spin-polarized atomic hydrogen (H^\uparrow) in an open-ended helium-coated chamber, at densities up to 0.8×10^{17} atoms/cm³. At a field of 10 T and temperature of 0.3 K, confinement times as long as 4 h are achieved. A quantitative study of the confinement times as a function of magnetic field is in excellent agreement with the expected escape from the magnetic potential well accompanied by a very slow loss process. Heat transport measurements confirm that the H^\uparrow is a gas and an upper limit is placed on the three-body recombination rate.

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Interest in spin-polarized hydrogen (H^\uparrow) has accelerated, spurred by theoretical studies of its unique properties as a quantum fluid¹⁻³ and by growing awareness of experimental possibilities for its production.^{4,5} An important experimental advance was achieved recently by Silvera and Walraven^{6,7} who verified that the surface recombination of H^\uparrow could be avoided by using a helium-coated surface and demonstrated stabilization of small amounts of H^\uparrow . We report here first results of a technique which allows much higher accumulation rate, density, and storage time than have yet been achieved, and which may open the way to study of H^\uparrow as a quantum fluid.⁸

The major experimental problems are to spin select the hydrogen atoms with essentially 100% efficiency, to stabilize them against spin relaxation, and to compress them to high density. Our approach rests on the use of a "magnetic bottle" to accomplish all three tasks simultaneously.⁵ The "bottle" consists of a low-temperature chamber covered with a helium film in a high magnetic field. The entrance to the chamber, an open tube, leads to a high-flux source of low-temperature atoms outside of the field. Atoms in the upper hyperfine states are repelled but those in the lower hyperfine states are drawn into the chamber by the magnetic force. Their excess kinetic energy is rapidly lost to the walls and they become trapped in the "bottle." We should emphasize that confinement is effected purely by the magnet-

ic field, in contrast to the helium-vapor-compressor (HEVAC) method of Silvera and Walraven which employs a flowing helium gas to help accumulate and confine the H^\uparrow . In our initial efforts we have obtained a density of approximately 10^{16} atoms/cm³, and have achieved confinement times of up to 4 h. Heat transport measurements confirm that the H^\uparrow is in the gas phase.

An important element of our technique is a high-flux source of atomic hydrogen at liquid-helium temperature. Such a source was developed and used to study the behavior of H on frozen H₂ surfaces in work reported earlier.⁹

Operation of our apparatus can be understood by referring to Fig. 1. Molecular hydrogen is dissociated in an rf discharge tube which is immersed in liquid nitrogen. The atoms pass through an orifice into a 4.2-K chamber whose walls are coated with frozen H₂. A baffle assures that the atomic hydrogen is thermalized at 4.2 K before it can proceed upwards to the cell. The cell is a 9.5-mm-diam hole in a 16-mm-diam copper rod. The hole ends near the midplane of the superconducting magnet, but the rod continues upwards to the mixing chamber of a dilution refrigerator. A gap of less than 1 mm separates the tip of the copper rod from the exit of the 4.2-K baffle. With this geometry the hydrogen atoms encounter only solid H₂ walls at 4.2 K or superfluid ⁴He walls at about 0.3 K. Vacuum integrity is maintained by a concentric stainless-steel tube which connects