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$T_{1\rho}$ measurements of hydrogen diffusion in titanium hydride

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Spin-lattice relaxation time ($T_{1\rho}$) of hydrogen in $TiH_{1.81}$ and $TiH_{1.90}$ was measured as a function of temperature yielding hydrogen diffusion parameters. The activation energy is equal to 11.7 ± 0.3 kcal/mole over more than six orders of magnitude of the jump frequency with a break occurring in the Arrhenius relation at 270 K. Discrepancies were found in the preexponential factor and the conduction-electron relaxation times as measured by T_1 and $T_{1\rho}$.

The theory of hydrogen diffusion in metals contains unique aspects and quantum effects not found for other atoms due to the small mass of the hydrogen atom.[1] Inconsistencies with classical rate behavior have been generally discussed with respect to bcc metals such as Nb and V whose activation energies are smaller than the localized hydrogen vibration energy.[2] The small-polaron hopping model predicts an Arrhenius law for $T \geqslant \Theta_{\mathrm{Debye}}$ (~250 K) with deviations occurring below this temperature.[1] Although breaks in the Arrhenius behavior near 250 K have been reported for Nb and Ta,[3] Kehr[1] has rejected this theory as describing diffusion in these metals because of inconsistencies found for isotope effects. Invalidating the Condon approximation for the case of hydrogen diffusion, Emin *et al.*[4] and Teichler[5] have extended the quantum-hydrogen-diffusion theory showing that it is consistent with the isotope effect and suitably describes the change in activation energy observed for H in Nb and Ta at 250 K. While Emin *et al.* deal with bcc metals, Teichler has developed an expression for fcc metals which shows that above a temperature T_0, over-the-barrier transitions predominate while below this temperature tunneling is the major diffusion mechanism. Estimates for the fcc metal Cu give $T_0 \approx 150$ K for octahedral-tetrahedral-octahedral jumps, but the experiments were performed above 700 K so that no experimental evidence for hydrogen diffusion anomalies in fcc metals have been reported.

Hydrogen in the fcc phase of titanium hydride diffuses with the relatively high activation energy of about 0.5 eV,[6] and neutron inelastic scattering studies[7] have resolved three nearly equally spaced optical levels 0.142 eV apart. By measuring the NMR spin-lattice relaxation time in the rotating frame ($T_{1\rho}$), we have been able to extend the diffusion results[6] down to lower temperatures. The results show that while the activation energy remains constant over more that six orders of magnitude, a break in the Arrhenius plot occurs at about 270 K. Also, discrepancies were found in the preexponential factor and the conduction-electron relaxation times as measured by T_1 and $T_{1\rho}$.

$T_{1\rho}$ of hydrogen in $TiH_{1.81}$ and $TiH_{1.90}$ was measured at a resonance frequency of $\omega_0/2\pi = 17.13$ MHz and rotating field $H_1 = 15.4$ G as a function of temperature using the same samples employed in Ref. 6 where T_1 was obtained. The measurements were extended down to temperatures where the sole relaxation mechanism is that due to the conduction electrons, facilitating the separation of the electronic and diffusional contributions to the relaxation rate. The results are shown in Fig. 1.

The low-temperature data yielded values of $(T_{1\rho})_e T$ equal to 46.6 and 46.3 sec K for $TiH_{1.81}$ and $TiH_{1.90}$, respectively, so that $(T_{1\rho})_d$, the diffusional relaxation rate, is obtainable through the relation $T_{1\rho}^{-1} = (T_{1\rho})_e^{-1} + (T_{1\rho})_d^{-1}$. Since for our case $H_1^2 \gg \frac{1}{3}M_2$ where M_2 is the second moment, weak collision theory is applicable. Assuming an exponential correlation function where the reciprocal of the correlation time is taken to be equal to the hydrogen jump frequency ν, one obtains[8]

$$(T_{1\rho})_d^{-1} = \frac{4}{3}(T_{1\rho})_{d,\min}^{-1}\left(\frac{3y}{y^2+4}+\frac{5y}{y^2+a^2}+\frac{2y}{y^2+4a^2}\right), \qquad (1)$$

where $(T_{1\rho})_{d,\min}$ is the minimum value of $(T_{1\rho})_d$, $y = \nu/\omega_1$, $\omega_1 = \gamma H_1$, γ is the gyromagnetic ratio, and $a = \omega_0/\omega_1$. The applicability of this equation can be checked against

$$(T_1)_{d,\min}/(T_{1\rho})_{d,\min} = 0.263\omega/\omega_1 ,$$

where ω is the angular resonance frequency at which the T_1 results were obtained. In our case $\omega = 2\pi(19\times10^6)$ Hz (Ref. 6) so that $0.263\omega/\omega_1 = 76$. The experimental values of $(T_1)_{d,\min}/(T_{1\rho})_{d,\min}$ are $8.92/0.144 = 62$ and $8.55/0.111 = 77$ for $TiH_{1.81}$ and $TiH_{1.90}$, respectively. This represents fairly good agreement.

The temperature dependence of ν shown in Fig. 2 obeys an Arrhenius relation of the form $\nu = A\exp(-E_a/RT)$ where $E_a = 11.7 \pm 0.3$ kcal/mole for both samples and $A = 1.3\times10^{12}$ and 0.79×10^{12}

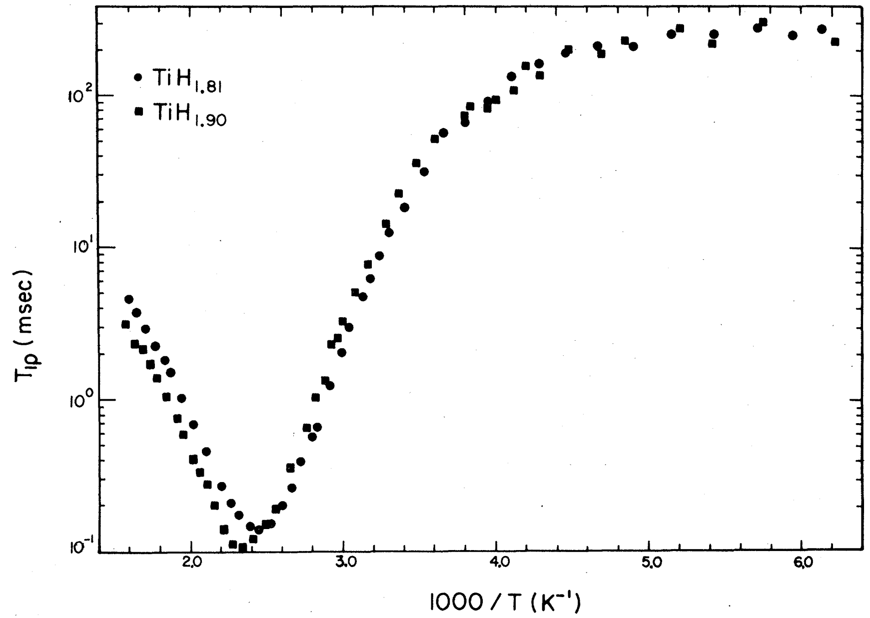

FIG. 1. Temperature dependence of spin-lattice relaxation time $T_{1\rho}$ in rotating frame.

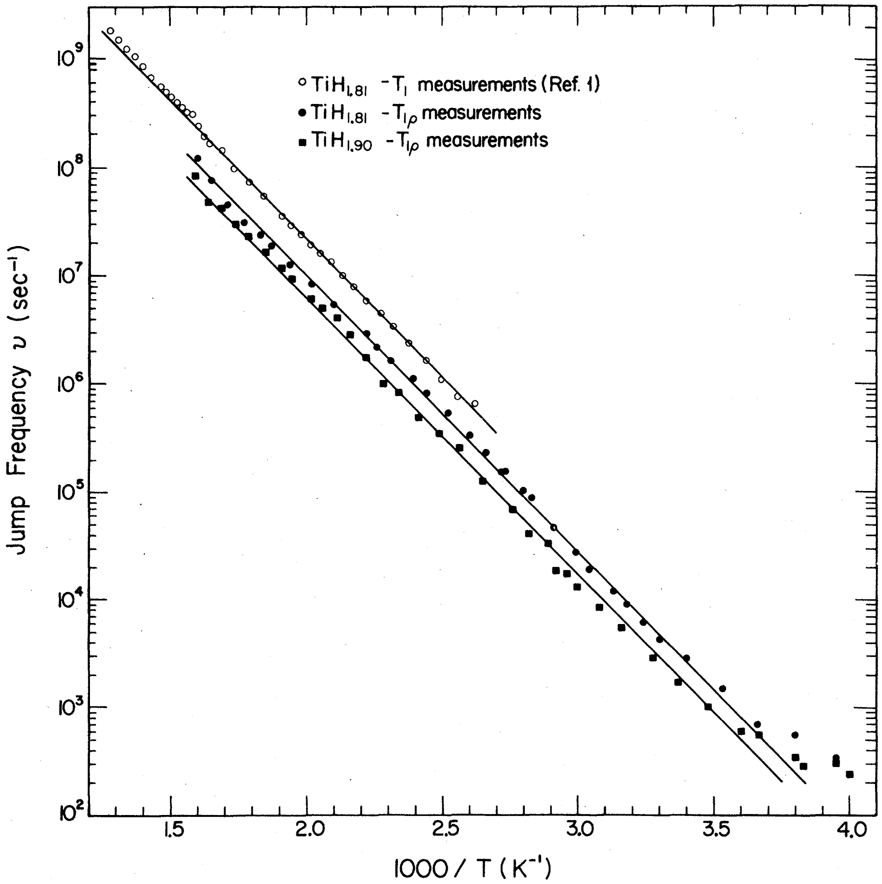

FIG. 2. Temperature dependence of diffusional jump of frequency ν obtained from $T_{1\rho}$. The straight lines through the experimental points are $\nu = A \exp(-11.7 \text{ kcal/mole}/RT)$ with A equal to 1.29×10^{12} and 0.793×10^{12}/sec for $TiH_{1.81}$ and $TiH_{1.90}$, respectively. Also shown are the results from T_1 for $TiH_{1.81}$ (Ref. 6).

sec^{-1} for $\mathrm{TiH}_{1.81}$ and $\mathrm{TiH}_{1.90}$, the lower value of A being due to fewer available vacancy jump sites. [A was shown to be proportional to the number of vacancies[6] which for our case is (2 − 1.81) and (2 − 1.90). This ratio is 1.63 while the ratio of the two values for A is 1.90 in fair agreement.]

Deviations from a constant activation energy are discerned for both samples for $1000/T$ above 3.6 K^{-1}. Even for the lowest temperature points shown in Fig. 2, diffusion accounts for approximately half of the relaxation rate, and at temperatures where the deviation from a constant E_a becomes apparent, diffusion accounts for about $\frac{2}{3}$ of the relaxation rate. Hence the effect is probably real. Nothing untoward has been found to occur at this temperature. Low-temperature x-ray diffraction studies[9,10] and second moment NMR studies[11,12] do not reveal any phase changes or hydrogen reorientation to occur except for the well-known small tetragonal distortion occurring at about 310 K. One is therefore tempted to ascribe the break in the Arrhenius relation to quantum effects predicted for hydrogen diffusion in this temperature range.[4,5]

There is considerable overlap in the temperature range of this study with that in Ref. 6. A comparative study[13] shows that E_a is relatively independent of the model used to describe the correlation function, while A can differ by a factor of about 2. Since, however, identical theories were used for both studies, one would expect coincidence of the results. Nevertheless, it was found that although both studies gave the same activation energy, ν derived from the T_1 data is about twice that obtained here from $T_{1\rho}$. This is illustrated in Fig. 2 for the $\mathrm{TiH}_{1.81}$ sample. It is as if each jump is twice as effective in relaxing the dipolar energy compared to the Zeeman energy. Although unusual frequency dependencies have been reported,[14,15] these are generally connected to complications in molecular reorientation processes where a possible distribution of barrier heights exists. On the other hand, T_1 measurements in TiH_x at various frequencies[6,16,17] do not show an anomalous behavior. It is only in going from T_1 to $T_{1\rho}$ that the problem arises. It should be noted that a Monte Carlo analysis of the data of Ref. 6 yielded an activation energy as much as 9% higher than the 11.7 kcal/mole we report.[18]

The respective $(T_{1\rho})_e T$ values of 46.6 and 46.3 sec K obtained here differ considerably from 69 and 67 sec K for $(T_1)_e T$.[19] The relation between $(T_{1\rho})_e$ and $(T_1)_e$ is given by[20]

$$\frac{(T_1)_e}{(T_{1\rho})_e}=\frac{\lambda H_1^2+\delta H_L^2}{H_1^2+H_L^2}, \tag{2}$$

where $3H_L^2$ is the second moment which equals 24 G^2 (Ref. 21) and $\lambda=1$ (Ref. 22) and $\delta=2$ (Ref. 23) for metals. Hence we should have $(T_{1\rho})_e=(T_1)_e$ within experimental error. Experimental difficulties prevented us from checking $(T_{1\rho})_e$ at lower H_1, but when H_1 was raised from 15.4 to 30.6 G, no change in $(T_{1\rho})_e$ was observed; hence H_1 was definitely large enough to make the ratio in Eq. (2) equal unity. Indeed, the fact that $(T_{1\rho})$ at low enough temperatures remained the same upon doubling H_1 showed that we reached low enough temperatures where diffusion does not contribute to the relaxation. Similarly, in the low-temperature T_1 measurements, T_1 remained the same when the resonance frequency was doubled from 25 to 50 MHz. Hence no atomic kinetics are involved in the relaxation at low temperature; only the conduction electrons are responsible. When an attempt was made to remove the electronic contribution from $T_{1\rho}$ using T_{1e} rather than the low-temperature $T_{1\rho}$ values, an unrealistic $\ln\nu$ vs $1000/T$ relation was obtained. Thus the inconsistency between T_{1e} and $(T_{1\rho})_e$ is real and an inexplicable value of $\lambda=1.5$ would be necessary to remove the discrepancy. Ailion and Slichter[24] also found a discrepancy between the experimental value of $(T_{1\rho})_e$ and that predicted by Eq. (2) which they explained by paramagnetic impurities that relax the Zeeman energy but not the dipolar energy. A similar explanation is not applicable here.

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