THE EFFECT OF MAGNETIC IMPURITIES ON THE APPARENT DIFFUSION CO-
EFFICIENT OF HYDROGEN IN METAL HYDRIDES DEDUCED FROM NMR

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ABSTRACT

Observations of the well-known minimum in proton spin-lattice
relaxation time, $T_1$, as a function of temperature, $T$, caused by
diffusion-induced fluctuations of nuclear dipole-dipole inter-
actions, have often been used to determine hydrogen diffusion
coefficients, D, in metal-hydrogen systems. In several cases
the minimum has appeared asymmetric with a shallower low-temp-
erature slope interpreted as a change to a diffusion mechanism
with a lower activation energy. In a few cases a subsidiary low-
temperature minimum has been observed or inferred and interpreted
in terms of two coexisting mechanisms. We believe that these
complications are likely to be due to interaction with paramagnetic
impurities, analogous to the case of doped fast-ion conductors.
We have measured $T_1(T)$ for $^{1}H$ in YH$_{1.98}$ containing controlled
amounts of gadolinium and observed growth of the above features
with increasing impurity content, together with a low-temperature
region ($T_1$ independent of $T$) controlled by spin-diffusion, and
also the beginning of a third, high-temperature minimum not
previously found in metal-hydrogen systems. It is concluded
that some $D(T)$ values deduced from existing NMR data must be
treated with caution until measurements on specimens with con-
trolled impurity content are complete.

INTRODUCTION

Nuclear magnetic resonance has been used for many years to
investigate hydrogen diffusion in transition metals. In most cases
the proton spin-lattice relaxation time $T_1(T)$ passes through a
minimum when $\omega_0 \tau_c \sim 1$ and has been used to deduce the temperature
dependence of the correlation time $\tau_c$ (half the mean jump time $\tau_D$,
for proton-proton interactions), which is then fitted to an Arrhenius
relation to deduce the activation energy $E_a$. For many systems a
discontinuous change in $E_a$ has been found, usually on the low-
temperature side of the $T_1$ minimum, and sometimes an additional
minimum, perhaps only partially resolved, has been observed in the
same region. These effects are illustrated in fig. 1.

Similar behaviour has been seen in yttrium dihydride. In this
system the metal atoms form an f.c.c. lattice with $a_0 = 5.205\text{Å}$ and
the hydrogen atoms predominantly occupy tetrahedral interstitial
sites. However a significant octahedral site occupation at
temperatures as low as 160-200K has been deduced from NMR second
moment measurements in agreement with neutron experiments. A
non-Arrhenius behaviour of $\tau_c$ giving a discontinuity in $E_a$ and a
partially resolved double minimum in $T_1(T)$ have been interpreted as
due to different types of motion on the tetrahedral and octahedral
sublattices. In this paper we present some new observations of $T_1$

![Fig. 1. Variations of $\tau_c$ (A and B) and $T_1$ (C and D) with temperature in some metal hydrides.](image-url)