^{1}H PULSED NMR INVESTIGATION OF THE ZrCr$_2$H$_x$ HYDRIDES

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Proton relaxation times T_1 and T_2 were measured on the ZrCr$_2$H$_x$ hydrides as a function of the hydrogen concentration x in the temperature range between 180K and 380K. The spin-lattice (T_1) and spin-spin (T_2) relaxation times were obtained for the series ZrCr$_2$H$_x$ (x=2,3,4) at a resonance frequency of 33 MHz using the 180°-τ-90° pulse sequency and the Carr-Purcell-Gill-Meiboom pulse train, respectively. T_1 was found to decrease as the temperature was increased from 180K until about 240K, where a minimium in T_1 occurs. Thereafter T_1 increases until 480K, the higher temperature reached in our experiment. However an asymmetrical and nonlinear behaviour of $\ln T_1$ versus $1/T$ abour T_1-minimium was observed for all hydrides studied. T_2 increases as the temperature is increased until about 240K when the T_1 contribution to T_2 becomes important. Thereafter T_2 becomes amost temperature independent for higher temperatures. We associated these features to the superposition of two contributions to the neclear relaxation. The first contribution (T_{1d}) arises from the nuclear relaxation due to the protons diffusion. The second is the contribution from the interaction of the protons ^{1}H with the conduction electrons given by the Korringa relation $(1/T_{1e}) = C_k T$. These two contributions to the relaxation times were obtained by fitting the experimental T_1 and T_2 data to the BPP theory[1] assuming the relations $(1/T_1) = (1/T_{1d}) + (1/T_{1e})$ and $(1/T_2) = (1/T_2') + (1/T_1)$ where $1/T_{1d}$ and $1/T_2'$ are the BPP spin-lattice and spin-spin relaxations rates, respectively.

From the fitting procedure we have obtained the diffusional activation energy Ea and Korringa constant C_k for the several hydrides investigated: Ea/

K_B = 1500K, C_k = 180(10^{3}s.k)$^{-1}$ for ZrCr2H2; Ea/K_B = 1700K, C_k = 110 (10^3 s.k)$^{-1}$ for ZrCr2H3 and Ea/K_B = 1800 K, C_k = 77(10^3 s.k)$^{-1}$ for ZrCr2H4. Single value of Ea was found for each hydrogen concentration indicating that the diffusion mechanism in these hydrides can be caracterized by the Arrhenius relation τ = τo exp(Ea/K_BT). This result indicates that the H atoms are located at only one kind of sites (probabily the 2Zr, 2Cr sites) in the ZrCr$_2$H$_x$. This agrees with recent neutron diffraction results of Fruchart et al.[2] In addition the Korringa constant C_k which is proportional to $N^2(E_F)$, was seen to decrease as x increased, indicating a reduction in the electronic density of state at the Fermi level $N(E_F)$ in the ZrCr$_2$H$_x$ as the concentration of hydrogen atoms increases.

In summary, our NMR results have shown that the proton relaxation times in the ZrCr$_2$H$_x$ hydrides can be described by a superposition of two contributions: the diffusion relaxation mechanism of the hydrogen atoms and the Korringa mechanism that account for the conduction electrons contribution to the relaxation process. Using the simple BPP theory we were able to abtain the diffusional activation energy for the hydrides ZrCr$_2$H$_x$ (x=2,3 and 4). We have found Ea values which are consistant with the known experimental data for metallic hydrides in general. A detailed analysis of our NMR results for ZrCr$_2$H$_x$ will be made in a further paper.

1. N. Bloembergen, E.M. Purcell and R. V. Pound, Phys.Rev. 73,679 (1984)
2. D. Fruchart et al., J.L.C. Metals, 73,363 (1980)