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Quasi-elastic neutron scattering study of the hydrogen diffusion in the C15 Laves structure, $TiCr_{1.85}$

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Abstract

High-resolution quasi-elastic neutron scattering measurements have been performed on the hydride form of the C15 Laves phase compound, $TiCr_{1.85}$, using the IN10 backscattering spectrometer at the ILL, France. The broadened spectra were observed over the temperature range 313–442 K and over a range of momentum transfers from 0.15 to 1.82 $Å^{-1}$ for a concentration of $[H]/[M]=0.15$. Only a single Lorentzian convoluted with the resolution function was necessary to fit the data in the whole Q range, suggesting that the diffusion occurs via a single jump mechanism. Values of the tracer diffusion coefficient and the activation energy for diffusion have been extracted from the low-Q sections of the data, and the mean jump length has been determined. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Quasi-elastic neutron scattering; Laves phases; Hydrogen; Diffusion

1. Introduction

The hydrides of Laves phase compounds (C14 and C15 structures) generate much interest both from a scientific viewpoint, as examples of solid state diffusion systems, and commercially, as electrode materials for metal hydride batteries. In these structures, having the composition AB_2, there are several possible hydrogen sites, in particular tetrahedral sites g, e and b for which the nearest neighbour atoms are, respectively, A_2B_2, AB_3 and B_4. In $TiCr_{1.8}$ [1], the g site is most readily occupied and the e sites are only occupied at higher hydrogen concentrations than observed here.

$TiCr_{1.8}$ is an interesting compound in the sense that the C15 Laves phase is formed only in the non-AB_2 stoichiometric form which leads to a substitution of Ti atoms onto the Cr sites. Therefore, this compound will not only have g and e sites available for hydrogen, but also pseudo-g (g') and pseudo-e (e') sites. The g' site has approximately the same spatial geometry as the g site, but with the substitution of a Cr atom by a Ti atom ($g' \rightarrow$1Cr–3Ti) and similarly for e' site where substitution of a Ti atom into the Cr gives ($e' \rightarrow$2Ti–2Cr). However, where the substitution is made, the differences in the atomic size between the Ti and Cr will engender a difference in the size of the site. According to the Westlake criterion [1], the g site has the biggest radius, $r=0.36$ Å, and is therefore the first to be

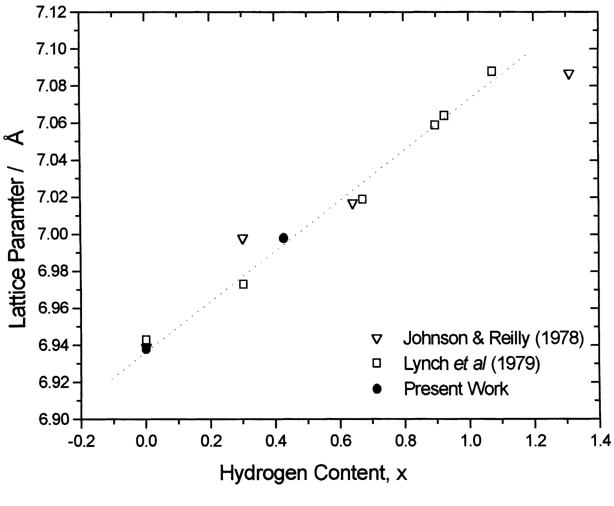

Fig. 1. The variation of the lattice parameter of $TiC_{1.85}H_x$ with hydrogen concentration, x. The dotted line is only shown as a guide for the eye.

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occupied upon hydrogenation. However, here, the g' site could be larger or smaller than the normal g site, due to the substitution of a larger atom (Ti) onto the site of a smaller atom (Cr). It is difficult to argue conclusively either way. If the g' site is bigger, we would expect it to be the more stable and hence preferentially occupied. We have calculated that there will be, on average, 5.04 g' sites per unit cell. Therefore, simultaneous occupancy of all the g' sites will give $[H]/[M]=0.074$, which is half the $[H]/[M]$ of the sample discussed here. However, it should be noted that simulataneous occupation of all the g' sites is unlikely as they will be localised around the substituted Ti sites and will therefore be too close for full occupation. If the g' site is occupied, the remaining H can be accomodated on the g sites, and hence the quasi-elastic line should have two components, one for each site. However, if the two sites are very similar it will be very difficult to establish two separate widths for the two components. On the other hand, if the g' site is the smaller, all the hydrogen could be accommodated in g sites.

The present work presents a quasi-elastic neutron scattering measurement on $TiCr_{1.85}H_{0.43}$, from which the elementary jump length, the microscopic tracer diffusion coefficient and the activation energy will be calculated.

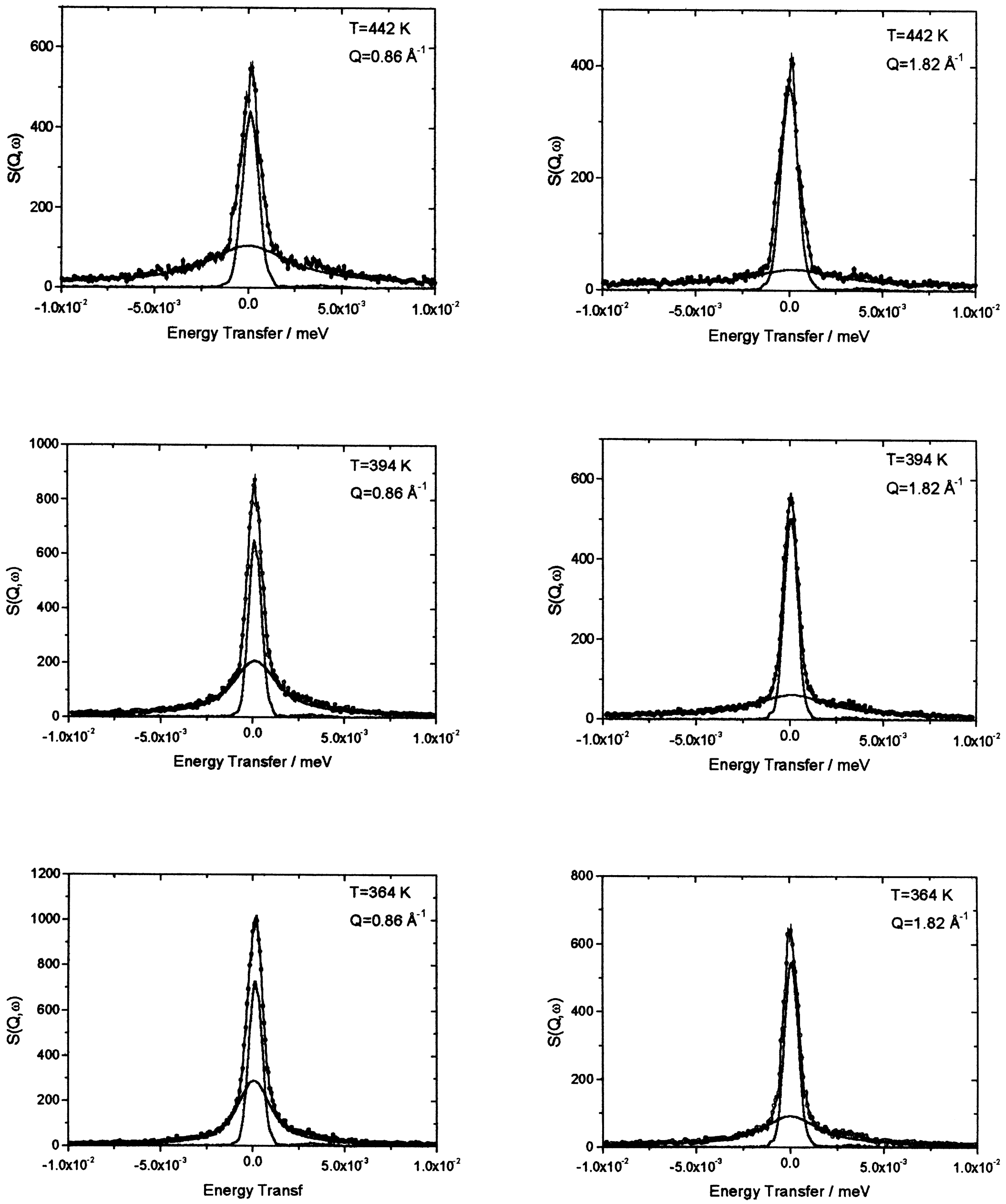

Fig. 2. Measured spectra for $TiCr_{1.85}H_{0.43}$ at two different values of the momentum transfer, Q, for three different temperatures.

2. Experimental details

The $TiCr_{1.85}$ alloys were made by melting the appropriate ratio of the constituent metals, of purity better than 99.95%, in an argon arc furnace. Before hydrogenation, the sample was annealed at 950°C under vacuum ($<10^{-6}$ mbar) for 15 days. The ingots were then hydrogenated at room temperature (hydrogen purity >99.999%) in a volumetric apparatus, to produce powdered samples with a particle size less than 75 μm. The hydrogen content was measured by observing the pressure drop in a calibrated volume. The cubic C15 Laves phase structure of the $TiCr_{1.85}$ sample before and after hydrogenation was verified by X-ray diffraction at room temperature. The variation of the lattice parameter as a function of hydrogen concentration can be seen in Fig. 1.

The quasi-elastic neutron scattering measurements were performed on the high resolution backscattering spectrometer, IN10, at the Institute Laue-Langevin, France. The measurements were made over a temperature range 313–442 K. The resolution function of the instrument was obtained using a vanadium plate at room temperature. In addition, measurements were made on an unloaded sample in order to provide an estimate of the elastic contribution from the metal. Multiple scattering corrections were made at a single temperature for the whole Q range using the DISCUS program [2]. The results showed that there was no noticeable multiple scattering from the sample within the experimental errors.

3. Results and discussion

Fig. 2 shows the quasi-elastic broadening at temperatures of 394, 364 and 442 K for momentum transfers of 0.86 and 1.82 $Å^{-1}$. The circles represent the experimental data. The fit to the data was achieved by convoluting a single Lorentzian with the resolution function, i.e. it was not necessary to use two Lorentzians. A flat background was also taken into account during the fitting process. The elastic contribution from the metal did not change as a function of temperature and its contribution to the total signal observed was of the same order of magnitude as for the unloaded sample. We can therefore assume that the elastic part of the quasi-elastic peak is entirely due to the host metal.

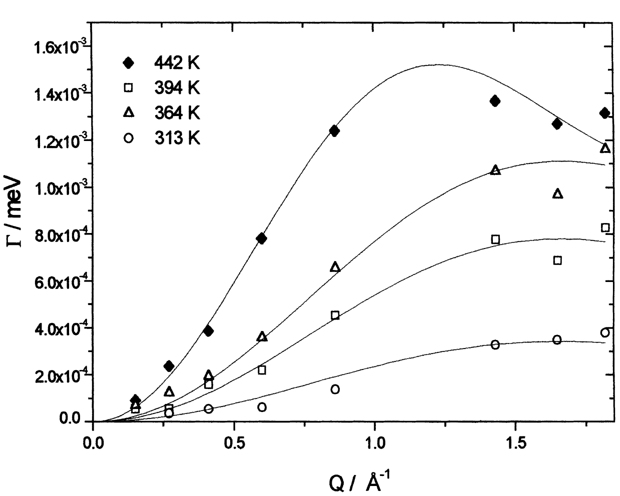

Fig. 3. Half width at half maximum vs. Q for four different temperatures. The solid line are fits to the Chudley–Elliot model.

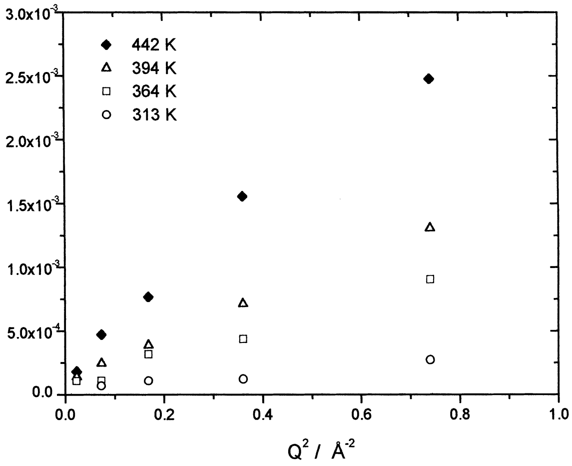

Fig. 4. Broadening as a function of Q^2 at low Q values for $TiCr_{1.85}H_{0.45}$

For the occupancy of two sites, as observed by Hempelmann et al. for $Ti_{1.2}Mn_{1.8}H_{2.9}$ [3], the peak at higher Q should break into two superimposed Lorentzians, with widths that asymptotically approach broadening of $\hbar/\tau$ for each site, where τ is the mean residence time for that kind of site. In our results, as mentioned above and as displayed in Fig. 2, only one Lorentzian was sufficient to fit the data. This suggests that only one type of site is occupied. However, as noted in the Introduction, we believe that the g and g' sites are both occupied. Therefore, we can only conclude that the substitution of the Ti onto the Cr site does not have a great effect on the diffusion mechanism. On the other hand, a different explanation can be given in

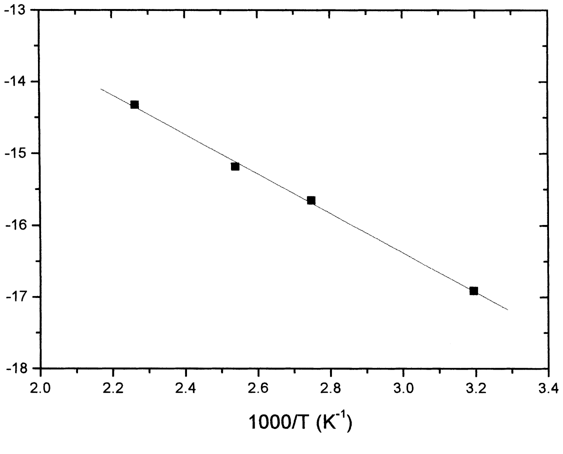

Fig. 5. Graph of the tracer diffusion vs. reciprocal temperature.

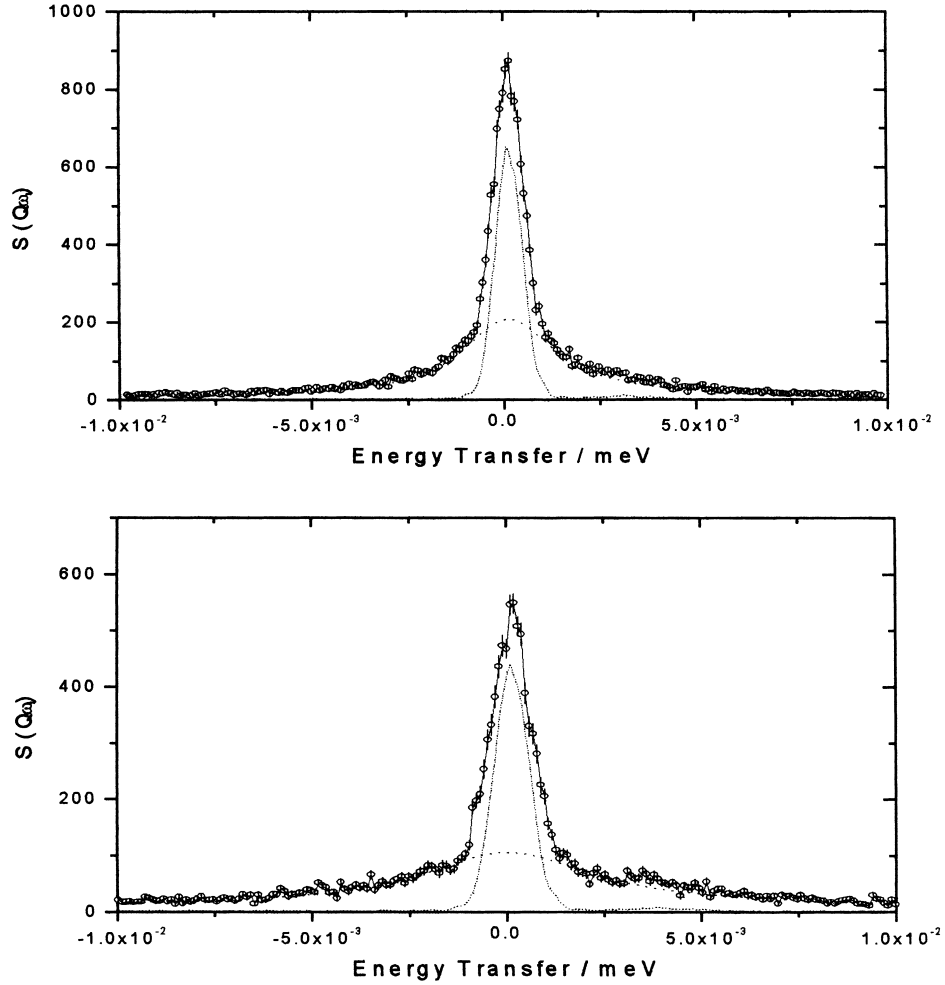

Fig. 6. Observed and fitted spectra for $TiCr_{1.85}H_{0.45}$ at Q=0.86 Å^{-1} at T=394 K (left) and at T=442 K (right).

which the g site is still more favorable, Thus, the g' and hence no g' sites are occupied. We believe this is rather unlikely due to the bigger size of g' and to the great affinity for hydrogen of Ti ($g'\rightarrow$1Cr–3Ti). Fig. 3 shows the broadening as a function of Q for four different temperatures. The solid lines represent the fit to the data using the polycrystalline version of the Chudley–Elliott model [4]. We first made a simultaneous fit to the four temperatures assuming the same jump length for all the temperatures. The fit led to a value for the effective jump length of 3.2±0.1 Å.

We have also fitted the data in a different manner, where the fit was carried out separately for each temperature, by varying both the residence time and the jump length, independently from the other temperatures. The jump lengths obtained were found to be approximately constant (l~2.70 Å) for temperatures up to 394 K, but increased to 3.62 Å at 442 K. The g sites form hexagonal rings [1], and we calculated the average distance between sites on two next nearest rings from which we obtained an average value of 3.64 Å. Therefore, we can explain our results in the following manner. For the lower temperatures, up to 394 K, the hydrogen is able to jump around the ring and between adjacent rings, while for the highest temperature, 442 K, the hydrogen makes subsequent jumps to the next nearest ring which explains the different value of the jump length, l=3.64 Å. It is, however, also possible that this effect is due to a structural phase change. We plan to perform diffraction measurements to ascertain whether this is the case. At low Q, a plot of the half width at half maximum (Γ) as a function of Q^2, Fig. 4, shows the expected linear relationship with a gradient of $\hbar D_t$ [5]. The tracer diffusion D_t calculated at room temperature, $D_t = 3.1\times10^{-8}$ cm^2 s^{-1}, agrees well within errors with the diffusion coefficient measured by NMR [6], $D_{NMR}=3.4\times$

Table 1
Comparison of the diffusion coefficient, jump rate and activation energies obtained on $TiCr_{1.85}H_x$ from different techniques

Techniques	QNS	NMR	INS
Sample	$TiCr_{1.85}H_{0.43}$	$TiCr_{1.8}H_{0.55}$	$TiCr_{1.85}H_{0.43}$
Temperatures (K)	313–442	190–280	30
E_a (eV)	0.24±0.02	0.19±0.02	0.27±0.06
D_t (cm^2 s^{-1}) at RT	3.1×10^{-8}	3.4×10^{-8}	–

10^{-8} $cm^2 s^{-1}$. The plot of $\ln(D_t)$ as a function of reciprocal temperature, Fig. 5, showed an Arrhenius dependence with an activation energy, $E_a = 0.24 \pm 0.02$ eV. This value fits well to the activation energy obtained for $TiCr_{1.8}H_{0.55}$ by NMR [2], Table 1. It also agrees, within the experimental errors, with the activation energy, $E_a = 0.27 \pm 0.06$ eV, calculated from our Born–Mayer model fitted to the inelastic neutron data measured on the same sample [7].

4. Conclusions

Quasi-elastic neutron scattering measurements have been performed on the C15 Laves phase compound, $TiCr_{1.85}H_{0.43}$. The average jump length obtained is 3.62 ± 0.01 Å at $T = 442$ K and 2.7 ± 0.01 Å for temperatures below 394 K. We have also obtained values for the diffusion coefficient of 3.1×10^{-8} $cm^2 s^{-1}$ at 300 K and for the activation energy, extracted from the low-Q region, of 0.24 ± 0.02 eV. These values agree well with other experimental techniques used on the same compounds.

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