

# diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

## Quasielastic Neutron Scattering Study of Hydrogen Diffusion in C14-Type $\text{ZrMn}_2\text{H}_3$

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### 1. Introduction

Hydrogen diffusion in Laves-phase intermetallic compounds  $\text{AB}_2$  shows a number of interesting features including high H mobility down to low temperatures, unusual isotope effects, and a coexistence of two frequency scales of H jump motion [1]. For the cubic (C15-type) Laves phases, the microscopic picture of H jumps and the systematics of the two frequency scales of H motion are well understood [1-3]. In most of the studied cubic Laves phases where H atoms occupy only tetrahedral interstitial sites of  $g$  type ( $\text{A}_2\text{B}_2$ ), the faster jump process corresponds to the localized H motion within the hexagons formed by  $g$  sites, and the slower process (leading to long-range diffusion) is associated with H jumps from one  $g$ -site hexagon to another. The difference between the characteristic frequencies of these jump processes is believed to result from the difference between the  $g$ - $g$  distances  $r_1$  (within the hexagon) and  $r_2$  (between the nearest hexagons). In contrast to the cubic Laves phases, the information on hydrogen diffusion in the hexagonal (C14-type) Laves phases is still fragmentary. The aim of the present work is to study the microscopic picture and the parameters of H jump motion in C14-type  $\text{ZrMn}_2\text{H}_3$  using quasielastic neutron scattering (QENS) measurements.

### 2. Results and discussion

QENS experiments have been performed on the time-of-flight neutron spectrometers FCS (with the incident neutron wavelengths  $\lambda = 4.8$  and  $4.08$  Å) and DCS ( $\lambda = 3.0$  Å) at the NIST Center for Neutron Research. In the temperature range 225 – 390 K the measured QENS spectra  $S_{\text{exp}}(Q, \omega)$  (where  $\hbar\omega$  is the energy transfer and  $\hbar Q$  is the elastic momentum transfer) can be reasonably described by a sum of three components: an ‘elastic’ line represented by the spectrometer resolution function and two resolution-broadened Lorentzian ‘quasielastic’ lines. The intensity of the broader quasielastic component is found to increase with increasing  $Q$ , and its half-width  $\Gamma_2$  appears to be nearly  $Q$ -independent. Since these features are typical of a spatially confined atomic motion, the broad quasielastic component is attributed to a fast localized H motion with the jump rate  $\tau_l^{-1}$  proportional to  $\Gamma_2$ . The half-width of the narrow quasielastic component,  $\Gamma_1$ , is found to increase with increasing  $Q$  and to pass through a broad maximum in the  $Q$  range  $2.4 - 3.0$  Å<sup>-1</sup>. Furthermore, the values of  $\Gamma_1$  rapidly increase

with increasing temperature. These features suggest that the narrow quasielastic component originates from a jump process leading to long-range H diffusion. The intensity of the elastic component is found to be small (about 9% of the total scattered intensity) and nearly  $Q$ - and  $T$ -independent. This component can be attributed to the residual elastic contribution due to the scattering on host-metal nuclei and, possibly, on some trapped protons.

The behavior of the narrow quasielastic component has been analyzed in terms of the orientationally averaged Chudley-Elliott model. The resulting rate of H jumps leading to long-range diffusion,  $\tau_d^{-1}$ , is found to follow the Arrhenius law in the temperature range 225 – 390 K with the pre-exponential factor  $\tau_{d0}^{-1} = (2.4 \pm 0.3) \times 10^{12} \text{ s}^{-1}$  and the activation energy  $E_a = 124 \pm 4 \text{ meV}$ . The values of the effective jump length  $L$  derived from the Chudley-Elliott fits are close to 1.7 Å, tending to increase slightly with increasing temperature. The values of  $L$  appear to be longer than the distances between the nearest-neighbor  $\text{Zr}_2\text{Mn}_2$  interstitial sites ( $\sim 1.2 \text{ Å}$ ) in  $\text{ZrMn}_2\text{H}_3$ ; this is consistent with the complex mechanism of H jump diffusion [1].

The structure of the sublattice of  $\text{Zr}_2\text{Mn}_2$  interstitial sites partially occupied by H atoms in  $\text{ZrMn}_2\text{H}_3$  [4] suggests two possible models of the fast localized motion: six-site jumps within the hexagons formed by these sites and two-site jumps between closely spaced sites. The observed  $Q$  dependence of the ‘resolution-limited’ elastic incoherent structure factor (EISF) is consistent only with the two-site localized motion corresponding to H jumps within a pair of the nearest-neighbor  $24l$  sites; the distance between these sites is 1.16 Å. In the range 225 – 390 K, the temperature dependence of the jump rate  $\tau_l^{-1}$  deviates from the Arrhenius behavior, being considerably weaker than that of  $\tau_d^{-1}$ . The ratio of the jump rates for the two processes,  $\tau_d/\tau_l$ , changes from 5 at 390 K to 60 at 225 K.

### 3. Conclusion

The diffusive motion of hydrogen in  $\text{ZrMn}_2\text{H}_3$  can be described in terms of at least two jump processes with different characteristic frequencies. The faster jump process corresponds to the two-site localized H motion within pairs of the nearest-neighbor  $24l$  sites, and the slower process is associated with H jumps leading to long-range diffusion. This is the first time that a two-site localized H motion has been observed in a C14-type hydride.

### References

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