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Quasielastic Neutron Scattering Study of Hydrogen Diffusion in C14-Type $ZrMn_2H_3$

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1. Introduction

Hydrogen diffusion in Laves-phase intermetallic compounds 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 (A_2B_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 $ZrMn_2H_3$ 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 λ = 4.8 and 4.08 Å) and DCS (λ = 3.0 Å) at the NIST Center for Neutron Research. In the temperature range 225 – 390 K the measured QENS spectra $S_{exp}(Q,\omega)$ (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 Γ_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 τ_l^{-1} proportional to Γ_2. The half-width of the narrow quasielastic component, Γ_1, is found to increase with increasing Q and to pass through a broad maximum in the Q range 2.4 – 3.0 Å^{-1}. Furthermore, the values of Γ_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, τ_d^{-1}, is found to follow the Arrhenius law in the temperature range 225 – 390 K with the pre-exponential factor $\tau_{d0}^{-1} = (2.4\pm0.3)\times10^{12}$ s^{-1} and the activation energy E_a = 124±4 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 Zr_2Mn_2 interstitial sites (~1.2 Å) in $ZrMn_2H_3$; this is consistent with the complex mechanism of H jump diffusion [1].

The structure of the sublattice of Zr_2Mn_2 interstitial sites partially occupied by H atoms in $ZrMn_2H_3$ [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 24*l* sites; the distance between these sites is 1.16 Å. In the range 225 – 390 K, the temperature dependence of the jump rate τ_l^{-1} deviates from the Arrhenius behavior, being considerably weaker than that of τ_d^{-1}. The ratio of the jump rates for the two processes, τ_d/τ_l, changes from 5 at 390 K to 60 at 225 K.

3. Conclusion

The diffusive motion of hydrogen in $ZrMn_2H_3$ 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 24*l* 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.

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