



Lattice Dynamical Investigation on the Diffusion of Hydrogen Isotopes in HfTi_2

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Abstract

The Laves phases structure AB_2 type intermetallic compound HfTi_2 is accomplished of storing hydrogen and its isotopes. The eigen values and eigen vectors of the host system are computed using a Born-von Karman formalism. The mean square displacements of hydrogen isotope and its surrounding host crystal atoms are computed using scattering matrix formalism and green function method. Diffusion parameters of hydrogen isotopes are estimated using reaction coordinate approach incorporating the scattering matrix formalism and green function technique. The theoretically calculated results are comparable with the existing experimental results.

Keywords: HfTi_2 , eigen values, eigen vectors, mean square displacement, diffusion parameters, hydrogen isotopes, green function technique, scattering matrix formalism and reaction coordinates

1. INTRODUCTION

HfTi_2 belongs to AB_2 type intermetallic compound, which is capable of storing hydrogen and its isotopes in its interstitial positions. HfTi_2 has Laves phase structure having AB_2 type lattice in which A sub-lattice is cubic whereas B sub-lattice is tetrahedral sharing one [1]. The quadruple defect formation as well as the vapour pressure as function of temperature have been described in terms of Ising

model using the Bragg Williams approximation in Laves phases [2]. The location of hydrogen atoms in the compound HfTi_2H_x is determined [3] and the hydrogen occupancies are two types with tetrahedral positions of 32e sites (AB_2) and 96g sites (A_2B_2) in HfTi_2 . In this compound at $x=4.0$, the e site positions are 82.5% and g site positions are only 5.83% occupied and at $x=4.5$, the e site position are 67.5% and g site positions are only 15% are filled. Moreover, the hydrogen stabilized cubic Laves phases (λ phase) is observed at $x=4.0$. The hydrogen diffusion parameters in the hydrogen stabilized Laves phase compound $\text{C15} - \text{HfTi}_2\text{H}_x$ have been estimated using a pulsed field gradient Nuclear Magnetic Resonance method [4]. Using pulsed field gradient NMR technique, two types of jump mechanism were observed in $\text{C15} - \text{HfTi}_2\text{H}_x$ on different time scales: long range diffusion from e site to e site through intermediate g-site and a fast localized motion [5]. Using the effective pair potentials for Ti, Zr, Hf, V, Nb, Ta and their hydrides from the first principle by inverting the ab initio inverted pair potentials, the elastic constants, bulk modulus and thermal properties of these hydrides are estimated [6]. Through X-ray diffraction study, it is observed that there is formation of a single hydrogen stabilized λ -phase in HfTi_2H_x at $x=4.0$ and 4.5 [7]. Though there are

few experimental studies dealing with the diffusion of hydrogen in this intermetallic compound, there are no theoretical studies except hydrogen diffusion in nanostructured HfTi₂ using green's function approach in this direction [8]. Hence, in this study, theoretically calculated values of defect modes, Debye Waller factor of host atoms surrounding hydrogen and the diffusion parameter of hydrogen isotopes are reported.

2. METHOD OF CALCULATION

The diffusion parameters of ¹H, ²H and ³H in this system are estimated using a green's function approach considering scattering matrix formalism and reaction coordinate method. To calculate the green's function values of the host material HfTi₂, its complete phonon spectrum is needed. The phonon spectrum of HfTi₂ is estimated using Born Von Karman formalism considering interaction up to six neighbors.

The force constant parameters used for the estimation of phonon spectrum of HfTi₂ are calculated using a Long-Range Empirical potential with parameters [9 & 10] and are arranged in table-1.

Table 1. Force constant values in 10⁴ dynes cm⁻²

A ₁₁ =-0.1868	A ₂₁ , A ₃₁ =4.5629	A ₂₃ =-0.0672	A ₃₁ = 4.5629	A ₄₁ , A ₆₁ 4.535	A ₅₁ =4.535
B ₁₁ = -0.1868	B ₂₁ =-1.4109	B ₂₃ =-0.093	B ₃₁ = -1.4109	B ₄₁ , B ₆₁ =4.535	B ₅₁ =4.535
C ₁₁ = 0.1526	C ₂₁ =0.5041	C ₂₃ =-0.033	C ₃₁ = 0.5041	C ₄₁ , C ₆₁ =-0.991	C ₅₁ = -0.9918
A ₁₂ = -0.1239	D ₂₁ =0.5041	D ₂₃ =0.0085	D ₃₁ = 0.5041	A ₄₂ , A ₆₂ =-0.088	A ₅₂ = -0.2193
B ₁₂ = 0.1795	A ₂₂ = -0.6177	E ₂₃ = -0.0046	A ₃₂ = -6.177	B ₄₂ , B ₆₂ = -0.088	B ₅₂ = -0.01582
A ₁₃ = -0.0026	B ₂₂ = -0.1574	E ₃₃ = -0.0046	B ₃₂ = -0.1574	C ₄₂ , C ₆₂ =0.0343	C ₅₂ = 0.097
B ₁₃ = -0.0026	C ₂₂ = 0.1363	F ₂₃ = -0.0041	C ₃₂ = 0.1363	A ₄₃ , A ₆₃ =-0.099	D ₅₂ = 0.176
C ₁₃ = 0.0005	D ₂₂ =0.1363	B ₃₃ = -0.093	D ₃₂ = 0.1363	B ₄₃ , B ₆₃ =0.0381	A ₅₃ = -0.0992
A ₃₃ = -0.0672	D ₄₃ , D ₆₃ = -0.0275	C ₃₃ = 0.033	D ₃₃ = 0.0085	C ₄₃ , C ₆₃ = 0.0153	B ₅₃ = 0.0381
	F ₃₃ = -0.0041		D ₅₃ = 0.0152		C ₅₃ = 0.0275

In order to calculate the defect modes and amplitudes of vibration of host crystal atoms and the defects, which involved in the estimation of reaction coordinates, one has to calculate the green's function values using the equation [11].

$$G_{\alpha\beta} \left(\begin{matrix} l & l' \\ k & k' \end{matrix}; \omega^2 \right) = \frac{1}{N \sqrt{m_k m_{k'}}} \sum_{q'} \frac{e_{\alpha}(k|\vec{q}) e_{\beta}(k'|\vec{q})}{\omega_{\max}^2} \exp \left[i \vec{q} \cdot (\vec{r}(l) - \vec{r}(l')) \right] \quad \dots (1)$$

where ω_{\max} is the maximum frequency among all normal modes of the crystal.

The defect modes are estimated using the green's function values by solving the secular equation,

$$\Delta(\omega^2) = |I - g(\delta I + a\gamma a^T)| = 0 \quad \dots (2)$$

where I, g, a, δI and γ respectively are the unit, green's function, change in dynamical, interaction of hydrogen with neighbors and interstitial green's function matrices. The displacement of neighboring atoms to the hydrogen isotope is computed using the equation

$$u_1 = \{I + g(\delta I + a\gamma a^T) [I - g(\delta I + a\gamma a^T)]^{-1} \} \dots (3)$$

$$\text{where } u_{\alpha} \left(\begin{matrix} l \\ k \end{matrix}; \vec{q} \right) = \left\{ \frac{\hbar}{2Nm_k \omega_{qj}} \right\} e_{\alpha}(k, qj) \exp \left[i \vec{q} \cdot \vec{r} \left(\begin{matrix} l \\ k \end{matrix} \right) \right]$$

with ω_{qj} and $e_{\alpha}(k, qj)$ as phonon frequencies and eigen vectors respectively.

The displacement of hydrogen isotope is computed using the equation

$$\xi = -\gamma a^T u_1 \quad \dots (4)$$

In the jump process of hydrogen isotope, the jump is initiated as a result of fluctuation in the energy and momentum of the hydrogen isotope assisted by the phonon created by lattice vibrations. The reaction coordinate is estimated using the equation

$$\chi = \left(\xi_d - \frac{1}{m} \sum_j \vec{u}_j \cdot \vec{x} \right) \quad \dots (5)$$

where $\vec{\xi}_d$ and \vec{u}_j are displacements of diffusing atom and host atoms respectively.

Using the reaction coordinate, the jump frequency is computed using the equation [12 & 13]

$$\Gamma = \frac{\left(\sum_{\vec{q}, \alpha} \left[\omega^2(\vec{q}, \alpha) | \chi(\vec{q}, \alpha) | \right]^2 \right)^{-1/2} \exp \left[-\chi^2 / \sum_{\vec{q}} | \chi(\vec{q}, \alpha) | \right]}{\left(\sum_{\vec{q}, \alpha} | \chi(\vec{q}, \alpha) | \right)} \dots (6)$$

From this equation, Γ_0 is identified as

$$\Gamma_0 = \frac{\left(\sum_{(\vec{q}, \lambda)} \left[\omega^2(\vec{q}, \lambda) | \chi(\vec{q}, \lambda) | \right]^2 \right)^{-1}}{\left(\sum_{(\vec{q}, \lambda)} | \chi(\vec{q}, \lambda) | \right)^2}$$

Using the Golden rule

$$\Gamma = \Gamma_0 \exp\left[-\frac{E_a}{k_B T}\right] \quad \dots (7)$$

the activation energy E_a is calculated.

The pre-exponential factor of diffusion constant D_0 is calculated using the formula

$$D_0 = \frac{\Gamma_0 l^2}{6} m^2 s^{-1} \quad \dots (8)$$

3. RESULTS AND DISCUSSION

a) Eigen values and eigen vectors

The computed force constant values have been substituted in the dynamical matrix to calculate eigen values and eigen vectors by diagonalising the dynamical matrix for 84 wave vector points obtained by uniformly dividing the Brillouin zone [14].

b) Mean Square Displacement

The presence of interstitial hydrogen alters the displacement of nearby host atoms. The mean square displacement values for different temperatures are calculated and are compared with defect free situation as shown in fig. 1. It increases with temperature as expected. More over the MSD values of atoms surrounding 1_1H , 2_1H and 3_1H defects are decreased drastically. This may be due to the creation of resonance modes. During the resonance nodes of vibration, the vibrational amplitude of hydrogen isotope is expected to be high with the expense of that of the surrounding atoms.

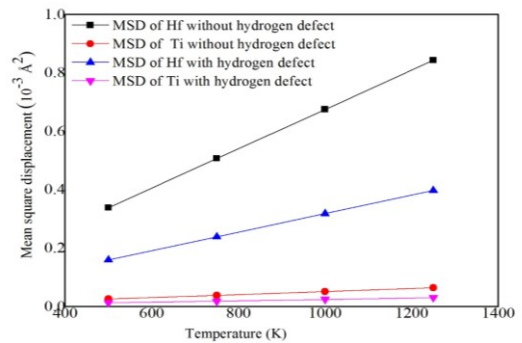


Figure 1(a). Mean square displacement of atoms surrounding the H-defect

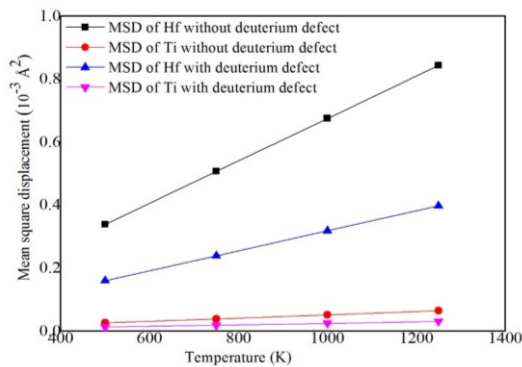


Figure 1 (b). Mean square displacement of atoms surrounding the $^1H_2^-$ defect

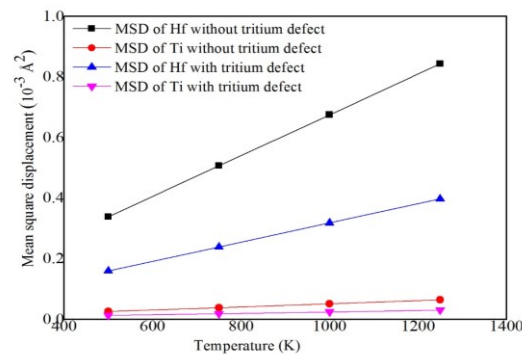


Figure 1(c). Mean square displacement of atoms surrounding the $^1H_3^-$ defect

c) Jump frequency values

Using green's function values and the change in dynamical matrix due to the presence of hydrogen and their isotopes (H, D and T) the jump frequency values were calculated using reaction coordinate

technique for different temperatures and these values are given in table 2. From this table, it is clear that jump frequency values increase with increase in temperature as expected.

Table 2. Jump frequency values at different temperature

Isotopes	Temperature (K)	Jump frequency $\Gamma \text{ sec}^{-1}$
$^1\text{H}^1$	500	3.05E+11
	750	1.37E+12
	1000	2.93E+12
	1250	4.62E+12
$^1\text{H}^2$	500	2.83E+11
	750	1.31E+12
	1000	2.82E+12
	1250	4.48E+12
$^1\text{H}^3$	500	2.76E+11
	750	1.29E+12
	1000	2.79E+12
	1250	4.44E+12

d) Diffusion parameters

The $\ln\Gamma$ versus reciprocal of temperature curve is as shown in fig. 2, which was found to be a straight line. From the intercept and slope, the pre exponential value of jump frequency Γ_0 and activation energy E_a values are determined. The D_0 value was calculated using the Eqn.

$$D_0 = \frac{\Gamma_0 l^2}{6} \quad \dots (4.1)$$

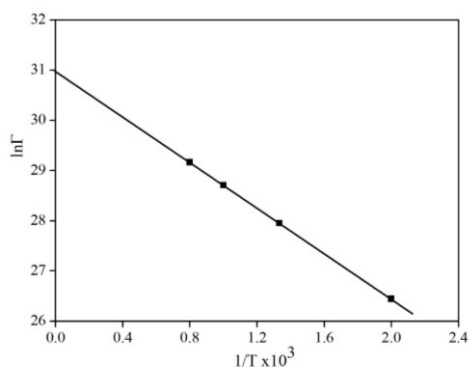


Figure 2 (a). Logarithmic of Jump frequency vs. $1/T$ for $^1\text{H}^1$ in HfTi_2

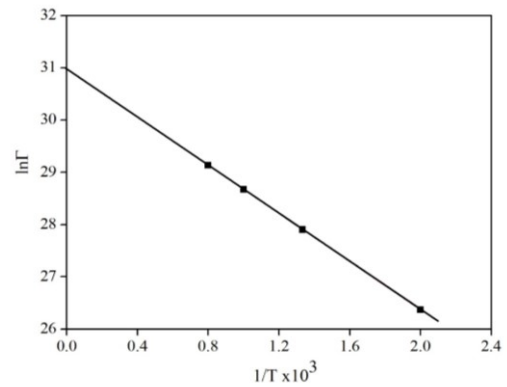


Figure 2 (b). Logarithmic of Jump frequency vs. $1/T$ for $^1\text{H}^2$ in HfTi_2

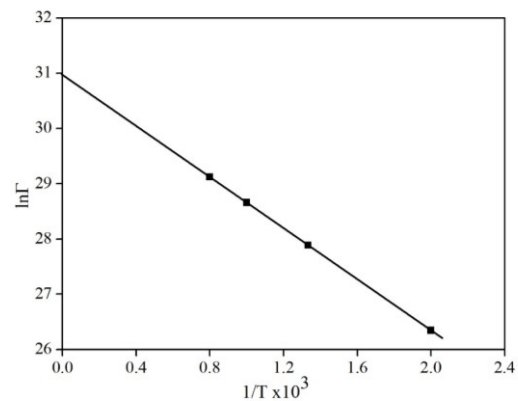


Figure 2 (c). Logarithmic of Jump frequency vs. $1/T$ for $^1\text{H}^3$ in HfTi_2

Our results are compared with that computed employing Quasielastic neutron scattering [3] and NMR studies [4] [5] in table 3. Our result is found to be comparable with the experimental results. Since the activation energy is very low of the order of 226 meV, there is no formation of permanent hydrides. As a consequence, it is easy to retrieve the hydrogen isotope back. Hence this system is a good candidate to store hydrogen and its isotopes.

Table 3. Experimental values of diffusion parameters of H in HfTi₂

Diffusing atom	Pre-exponential factor D ₀ (10 ⁻⁸ m ² sec ⁻¹)	Activation energy E _a (meV)	Reference
¹ H ¹	6.7081	226.4	This study
¹ H ²		230.1	
¹ H ³		231.3	
¹ H ¹	6.291	195	[8]
¹ H ¹	4.6 ± 1.6	230 ± 10	[3]
¹ H ¹	1.2 ± 0.3	210 ± 10	[4]
¹ H ¹	0.8	210	[5]

A comparative study is made as shown in table 4. Last two columns show that, D_{1H²}/D_{1H¹} and D_{1H³}/D_{1H¹} values are found to be less than one as expected. This result is in support for the application towards isotope separation.

Table 4. Comparative study

Temp. (K)	D _{1H¹}	D _{1H²}	D _{1H³}	Ratio D _{1H²} /D _{1H¹}	Ratio D _{1H³} /D _{1H¹}
500	9.96022E-31	4.21882E-31	3.42328E-31	0.42356704	0.343695221
750	4.0524E-23	2.28557E-23	1.98836E-23	0.564003032	0.490661892
1000	2.58484E-19	1.68227E-19	1.51538E-19	0.650820282	0.586255252
1250	4.95755E-17	3.5159E-17	3.23398E-17	0.709200222	0.652333073

4. CONCLUSION

A Born-von Karman formalism has been used to work out the eigen values and eigen vectors of the cubic Laves phased compound HfTi₂. The localized vibrational modes have been worked out with hydrogen atoms as an interstitial defect in this system. A green's function technique and scattering matrix formalism are used to work out the MSD values of hydrogen isotopes (¹H¹, ¹H² and ¹H³) and its neighbors at 500, 750, 1000 and 1250 K temperatures. A reaction coordinate technique has been used to work out the diffusion parameters of hydrogen isotopes (¹H¹, ¹H² and ¹H³) in HfTi₂. Estimated values are found to be in good agreement with the existing experimental results.

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study the crystal-to-amorphous phase transition.

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