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Hydrogen Diffusion in Nanostructured $HfTi_2$: A Green's Function Approach

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ABSTRACT

The Laves phases binary intermetallic compound $HfTi_2$ is one of the potential candidates for the storage of hydrogen. The knowledge on thermal properties of hydrogenated $HfTi_2$ is important in order to use this material for hydrogen storage application. This study has reported important thermal properties such as phonon frequency distribution, defect modes, mean square displacement and diffusion parameters of H in the hydrogenated $HfTi_2$ using lattice dynamical investigation involving green's function method and scattering of phonons by defect space atoms.

Key words: $HfTi_2$, phonon frequency distribution, mean square displacement, diffusion parameters, green's function method, scattering of phonons

INTRODUCTION

The study of hydrogen storage is important because of its relevance to the energy economy. Nowadays, the major energy needs of mankind are met by petroleum products, which may not be available for a long time. However, solar-hydrogen will alleviate the present energy crisis. Metals and alloys would be used to store hydrogen.

The binary intermetallic compound $HfTi_2$ has a Laves phases structure having composition AB_2 in which A sub lattice is a cubic diamond net whereas B sub lattice is tetrahedra sharing lattice (Johnston and Hoffmann, 1992). This intermetallic compound is a good solid hydrogen storage material. There is quadruple-defects formation in Laves phases (Modder and Bakker, 1997). The structure and phase composition interaction of the $HfTi_2$ alloy with hydrogen were investigated using X-ray diffraction (Kozhanov *et al.*, 1998; Nemnonov *et al.*, 2006). In their study it is found that hydrogen atoms occupy two types of tetrahedral interstitial positions: 32e (AB_3) and 96 g (A_2B_2) in $HfTi_2$. The e sites are 82.5% occupied and the g sites are 5.83% occupied by hydrogen atoms. It is also noticed that the order of the host lattice in the λ phase stabilized by hydrogen depends on the constant x. The high resolution quasi-elastic neutron scattering measurement on hydrogen stabilized phase $HfTi_2H_4$ has confirmed the existence of a fast localized hydrogen motion (Skripov *et al.*, 2000). The temperature increases the reaction of H atoms participating in the localized motion. Through pulsed-field-gradient nuclear magnetic resonance studies it is observed that the activation energy is found to vary with the concentration of hydrogen in $HfTi_2H_x$ (Eberle *et al.*, 2002).

Though there are few experimental studies dealing with the diffusion of hydrogen in this intermetallic compound, there are no theoretical studies in this direction. Hence, in this study, theoretically calculated values of defect modes, Debye Waller factor of host atoms surrounding hydrogen and the diffusion parameter of hydrogen are reported.

Method of calculation: To estimate the thermal properties of $HfTi_2H_4$, the first step is to calculate the phonon frequencies and eigen vectors. The phonon frequencies and eigen vectors of $HfTi_2$ are calculated using Born-von-Karman formalism considering interactions up to three neighbors. The dynamical matrix was constructed using force constants of the first neighbour interaction (A_{11}, B_{11}, A_{12}, B_{12}, C_{12}, D_{12}, A_{13}, B_{13}, C_{13}, D_{13}, A_{14}, B_{14} and C_{14}), second neighbour interaction (A_{21}, B_{21}, C_{21}, A_{22}, B_{22}, C_{22}, D_{22}, A_{221}, B_{221}, A_{23}, B_{23}, C_{23}, D_{23}, A_{231}, B_{231}, A_{24}, B_{24}, C_{24} and D_{24}) and third neighbour interaction (A_{31}, B_{31}, C_{31}, D_{31}, A_{32}, B_{32}, C_{32}, D_{32}, A_{33}, B_{33}, C_{33}, D_{33}, A_{34}, B_{34} and C_{34}), respectively.

By considering the C_{15} structure of $HfTi_2$ coordinates of the system of study and applying the Long-Range Empirical potential (Liang *et al*., 2010; Cui *et al*., 2010), the force constant values were calculated and are listed in Table 1.

The Green's function method is an effective mathematical tool for the estimation of the defect modes and the amplitude of vibration of the atoms affected by such defects. Green's function values are calculated using the Eq. 1 (Maradudin *et al*., 1971):

$$G_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix};\omega^2 = \frac{1}{N\sqrt{m_k m_{k'}}}\sum_{qj}\frac{e_\alpha(k|\vec{q}j)e^*_\beta(k'|\vec{q}j)}{\omega^2_{max}}\exp[i\vec{q}.(\vec{R}(l)-\vec{R}(l'))] \quad (1)$$

where, ω_{max} is the maximum frequency among all normal modes of the host crystal. The defect modes are obtained by solving the secular equation (Eq. 2) (Maradudin *et al*., 1971):

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

Table 1: Force constant values in 10^4 dynes cm^{-2}

Force constant	Value	Force constant	Value	Force constant	Value	Force constant	Value
A_{11}	1.1089	C_{31}	0.0002	B_{22}	0.0633	C_{32}	0.0061
B_{11}	1.1089	D_{31}	0.0002	C_{22}	-0.0333	D_{32}	0.0061
A_{21}	0.0233	A_{12}	2.3662	D_{22}	-0.0333	A_{13}	2.3662
B_{21}	0.0233	B_{12}	1.0368	A_{221}	0.068	B_{13}	1.0368
C_{21}	-0.0044	C_{12}	-0.3975	B_{221}	0.068	C_{13}	-0.3975
A_{31}	0.0054	D_{12}	-0.3975	A_{32}	0.0289	D_{13}	-0.3975
B_{31}	0.0019	A_{22}	0.2708	B_{32}	0.0214	A_{23}	0.2708
B_{23}	0.0633	C_{33}	0.0061	C_{24}	-0.0002		
C_{23}	-0.0333	D_{33}	0.0061	D_{24}	-0.0002		
D_{23}	-0.0333	A_{14}	4.8691	A_{34}	0.0015		
A_{321}	0.068	B_{14}	4.8691	B_{34}	0.0015		
B_{321}	0.068	C_{14}	-0.9602	C_{34}	-0.0002		
A_{33}	0.0289	A_{24}	0.0021				
B_{33}	0.0214	B_{24}	0.0011				

where, I is the unit matrix, g is the Green's function matrix, δl is the change in dynamical matrix, a is the matrix of interaction of hydrogen with neighbours and γ is the interstitial Green's function matrix. The elements of a matrix are calculated using the pair potential (Liu *et al*., 2002). The displacement of neighbouring atoms surrounding the interstitial is obtained using the Eq. 3:

$$u_l = \{I + g(\delta l + a\gamma a^T)[I - g(\delta l + a\delta a^T)]^{-1}\}u_\alpha \tag{3}$$

with u_α as:

$$u_\alpha\begin{pmatrix}1\\k\end{pmatrix};\vec{qj}\ \Big) = \left\{\frac{h}{2Nm_k\omega_{qj}}\right\}^{1/2} e_\alpha(k,\vec{qj})\exp\left[i\vec{q}.r\begin{pmatrix}1\\k\end{pmatrix}\right] \tag{4}$$

where, ω_{aj} are the frequencies of normal modes and $e_\alpha(k,\vec{qj})$ are the corresponding eigen vectors.

The mean square displacement values at a particular temperature T are calculated using the Eq. 5:

$$< u_l^2 >= \frac{1}{2}\int_0^\infty \frac{u_l^2(k,\omega_{\vec{qj}})}{\omega_{\vec{qj}}}\coth\left(\frac{h\omega_{\vec{qj}}}{2k_BT}\right)d\omega_{\vec{qj}} \tag{5}$$

Displacement of hydrogen atoms are calculated using the Eq. 6:

$$\xi = -\gamma a^T u_l \tag{6}$$

The γ matrix is of order of 3×3 which is defined as Eq. 7:

$$\gamma\left(\omega^2\right) = [m_i(\omega_j^2(q) - \omega_i^2)]^{-1} I\ s^{-1} \tag{7}$$

where, m_i is the mass of the interstitial atom and ω_i is the vibrational frequency of the H atom. The interstitial Green's function matrix γ has the form:

$$\begin{bmatrix}\gamma_1 & 0 & 0\\ 0 & \gamma_1 & 0\\ 0 & 0 & \gamma_2\end{bmatrix}$$

The hydrogen atom migrates by successive jumps, each jump involving an atom and its adjacent atoms. The jump is initiated as a result of fluctuation in the energy and momentum of the diffusing atom due to the lattice vibrations. The relative position of a diffusing hydrogen atom and that of neighbouring metal atom is essential to calculate the reaction co-ordinate. The reaction co-ordinate is written as Eq. 8:

$$\chi = \left(\bar{\xi}_d - \frac{1}{m}\sum_j \vec{u}_j\right).\hat{\xi} \tag{8}$$

with j = 1, 2, 3,... ., m and $\overline{\xi}$, the displacement of the diffusing atom and u_j, the displacement of the neighbour along the jump path.

The jump frequency is obtained using an approximation (Kac, 1943; Slater, 1959) as Eq. 9-11:

$$\Gamma = \left[\frac{\sum_{q,j}\omega^2(q,j)|\chi(q,j)|^2}{\sum_{q,j}|\chi(q,j)|^2}\right]^{\frac{1}{2}} \exp\left[-\frac{\chi_c^2}{\sum_{q,j}|\chi(q,j)|^2}\right] \tag{9}$$

$$\Gamma = \Gamma_0 \exp\left[-\frac{\chi_c^2}{\sum_{q,j}|\chi(q,j)|^2}\right] \tag{10}$$

with:

$$\text{with } \Gamma_0 = \left[\frac{\sum_{q,j}\omega^2(q,j)|\chi(q,j)|^2}{\sum_{q,j}|\chi(q,j)|^2}\right]^{\frac{1}{2}} \tag{11}$$

Equation 9 had been applied to atomic jump process (Rice, 1958; Glyde, 1967; Flynn, 1968; Seitz and Turnbull, 1960; Alefeld, 1964).

Equation 10 resembles the Golden rule (Eq. 12):

$$\Gamma = \Gamma_0 \exp(-E_a/k_B T) \tag{12}$$

where, E_a is the activation energy and k_B is the Boltzmann's constant.

The pre-exponential factor Γ_0 is an average of frequency values over the entire spectrum of fluctuation called attempt frequency of jump. Taking natural logarithm gives Eq. 13:

$$\ln\Gamma = \ln\Gamma_0 + (-E_a/k_B)\frac{1}{T} \tag{13}$$

Using Eq. 10, the Γ values at various temperatures are calculated. A graph connecting ln Γ versus 1/T is plotted. Form Eq. 13 it is clear that the intercept of this graph on the Y-axis gives lnΓ and the slope gives ($-E_a/k_B$) and hence activation energy E_a can be calculated. Knowing, Γ_0, E_a and the jump distance l, the diffusion co-efficient D can be calculated using the Eq. 14:

$$D = D0 \exp(-Ea/kB\ T) \tag{14}$$

where, the pre-exponential factor.

D_0 is calculated using the Eq. 15:

$$D_0 = \frac{\Gamma_0 l^2}{6}\ m^2\ s^{-1} \tag{15}$$

RESULTS AND DISCUSSION

The computed force constant values have been substituted in the dynamical matrix and the phonon frequencies and eigen v ectors were calculated by diagonalising the dynamical matrix for 84 wave vector points (Balaguru *et al*., 2002).

The phonon frequency distribution curve obtained is shown in Fig. 1. From this curve it is clear that more normal modes of vibration are distributed in the low and high frequency regions.

In the presence of defects, the individual frequency levels inside the bands of allowed frequencies by small amounts and a small number of frequencies which normally lie near the band edges can emerge out of the allowed bands into the gap of the forbidden frequencies. Such normal modes are called Localised Vibrational Modes (LVM) and they have frequencies greater than the maximum frequency of the host crystal. LVMs are observed due to light impurities or impurities which are tightly bound to the surrounding atoms. A special kind of LVM has been identified with the characteristics that its frequency falls in the gap of the two host crystal frequencies. Such modes are called gap modes. In addition to these two modes, resonance type mode occurs, for which, the vibrational amplitude of defect atom dominates that of host crystal atoms.

The defect modes present in $HfTi_2H_x$ are calculated using green's function method and scattering of phonons by defect space atoms. The maximum phonon frequency mode of $HfTi_2$ falls at 263.94 cm^{-1} and the estimated defect modes after the hydrogenation of $HfTi_2$ falls in the range of 324.36 to 438.84 cm^{-1}. The estimated LVM are listed in Table 2.

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. 2. It increases with temperature as expected. More over the MSD of atoms surrounding H defect is decreased drastically. This may be due to the creation of resonance

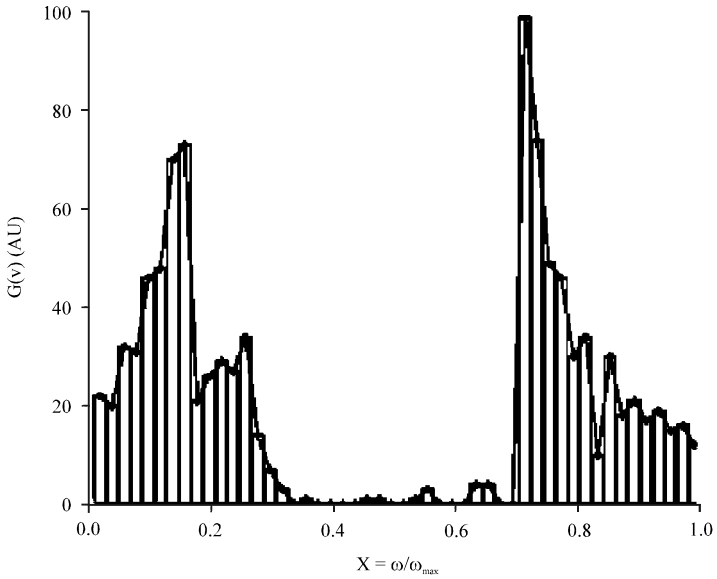

Fig. 1: Frequency distribution for $HfTi_2$

Table 2: LVM modes (cm^{-1})

324.36	367.82	378.42	391.14	425.59	438.84

Table 3: Jump frequency values at different temperatures

Temperature (K)	Jump frequency Γ (sec^{-1})
500	3.0516×10^{11}
750	1.3746×10^{12}
1000	2.9318×10^{12}
1250	4.6173×10^{12}

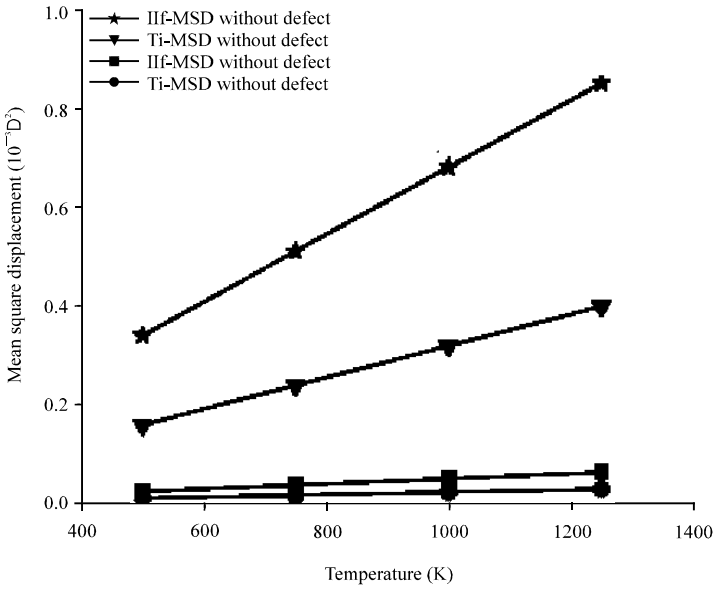

Fig. 2: Mean square displacement of atoms surrounding the H-defect

modes. During the resonance modes of vibration, the vibrational amplitude of hydrogen is expected to be high with the expense of that of the surrounding atoms.

Using Green's function values and the change in dynamical matrix due to the presence of hydrogen the jump frequency values were calculated using reaction coordinate technique for different temperatures and these values are given in Table 3.

The InΓ versus reciprocal of temperature curve is as shown in Fig. 3, which was found to be a straight line. From the intercept and slope, the Γ_0 and activation energy values are determined. The D_0 value was calculated using the Eq. 16:

$$D_0 = \frac{\Gamma_0 l^2}{6} \tag{16}$$

which is found to be $D_0 = 6.291\times10^{-8}$ m^2 sec^{-1}. E_a calculated from the slope is found to be 0.195 eV. Our results are compared with that computed employing Quasielastic neutron scattering (Skripov *et al.*, 2000) and NMR studies (Eberle *et al.*, 2002; Majer *et al.*, 2003) in Table 4. Our result is found to be comparable with the experimental results.

Table 4: Experimental values of diffusion parameters of H in $HfTi_2$

Pre-exponential factor D_0 (10^{-8} m^2 sec^{-1})	Activation energy E_a (meV)	Reference
6.291	195	This study
4.6±1.6	230±10	(Skripov *et al*., 2000)
1.2±0.3	210±10	(Eberle *et al*., 2002)
0.8	210	(Majer *et al*., 2003)

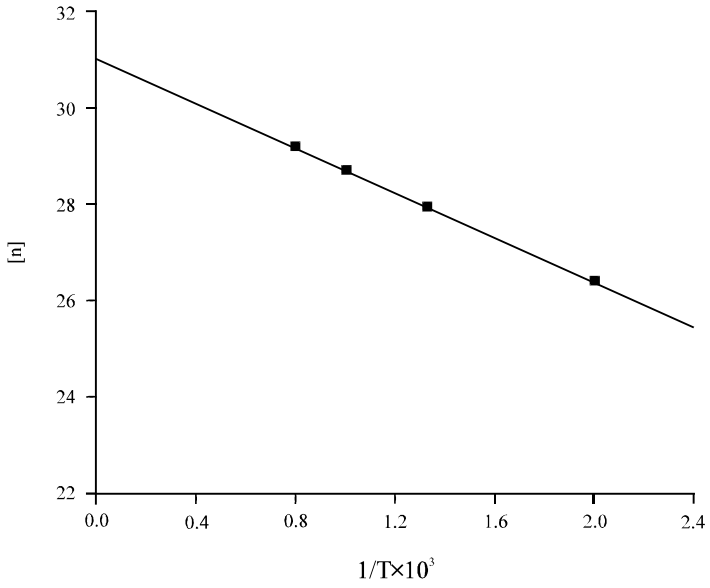

Fig. 3: Jump frequency vs. 1/T for H in $HfTi_2$

CONCLUSION

A Born-von Karman formalism has been used to work out the phonon spectrum of the cubic Laves phase compound $HfTi_2$. The localised vibrational modes have been worked out with hydrogen atom 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 H 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 H in $HfTi_2$ were estimated and the estimated values are found to be in good agreement with the related systems.

REFERENCES

Alefeld, G., 1964. Rate theory in solids at low temperatures. Phys. Rev. Lett., 12: 372-375.

Balaguru, R.J.B., N. Lawrence and S.A.C. Raj, 2002. Lattice Instability of 2H-$TaSe_2$. Int. J. Mod. Phys. B, 16: 4111-4125.

Cui, Y., J. Li, Y. Dai and B. Liu, 2010. Proposed truncated CU-HF tight-binding potential to study the crystal-to-amorphous phase transition. J. Applied Phys., Vol. 108. 10.1063/1.3477191

Eberle, U., G. Majer, A.V. Skripov and V.N. Kozhanov, 2002. NMR studies of hydrogen diffusion in the hydrogen-stabilized laves phase compound C15-$HfTi_2H_x$. J. Phys.: Condens. Matter, 14: 153-164.

Flynn, C.P., 1968. Atomic migration in monatomic crystals. Phys. Rev., 171: 682-698.

Glyde, H.R., 1967. Relation of vacancy formation and migration energies to the Debye temperature in solids. J. Phys. Chem. Solids, 28: 2061-2065.

Johnston, R.L. and R. Hoffmann, 1992. Structure-bonding relationships in the laves phases. Zeitschrift Anorganische Allgemeine Chemie, 616: 105-120.

Kac, M., 1943. On the distribution of values of trigonometric sums with linearly independent frequencies. Am. J. Mathe., 65: 609-615.

Kozhanov, V.N., A.V. Skripov and E.P. Romanov, 1998. Hydrogen in $HfTi_2$ alloy: A formation of the hydrogen-stabilized $HfTi_2H_x$ phase with the C15-type host lattice. J. Alloys Compd., 269: 141-143.

Liang, S.H., Y. Dai, J.H. Li and B.X. Liu, 2010. Glass forming region of Cu-TI-HF ternary metal system derived from the n-body potential through molecular dynamics simulation. J. Phys. Chem. B, 114: 9540-9545.

Liu, S.J., S.Q. Shi, H. Huang and C.H. Woo, 2002. Interatomic potentials and atomistic calculations of some metal hydride systems. J. Alloys Compd., 330-332: 64-69.

Majer, G., U. Eberle, F. Kimmerle, E. Stanik and S. Orimo, 2003. Hydrogen diffusion in metallic and nanostructured materials. Phys. B: Condens. Matter, 328: 81-89.

Maradudin, A.A., E.W. Montroll, C.H. Weiss and I.P. Ipatova, 1971. Theory of Lattice Dynamics in the Harmonic Approximation. Academic Press, New York, Pages: 708.

Modder, I.W. and H. Bakker, 1997. On quadruple-defect formation in C15 laves phases. Phys. Status Solidi B, 199: 369-378.

Nemnonov, S.N., V.M. Cherkashenko, V.N. Kozhanov, A.V. Skripov, E.Z. Kurmaev and E.P. Romanov, 2006. X-ray spectroscopic study of the electronic structure and location of hydrogen atoms in $HfTi_2H_x$ hydrides. Phys. Solid State, 48: 30-36.

Rice, S.H., 1958. Dynamical theory of diffusion in crystals. Phys. Rev., 112: 804-811.

Seitz, F. and D. Turnbull, 1960. Solid State Physics: Advances in Research and Applications. Vol. 10, Academic Press, New York, USA., ISBN-13: 9780126077100, Pages: 548.

Skripov, A.V., J. Combet, H. Grimm, R. Hempelmann and V.N. Kozhanov, 2000. Quasielastic neutron scattering study of H motion in the hydrogen-stabilized C15-type phases $HfTi_2H_x$ and $ZrTi_2H_x$. J. Phys.: Condens. Matter, 12: 3313-3324.

Slater, N.B., 1959. Theory of Unimolecular Reactions. Cornell University Press, New York, Pages: 230.