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Lattice Dynamical Investigation on the Diffusion of Hydrogen Isotopes in Mg_2Ni

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Abstract

Metals and alloys play a vital role in the storage of hydrogen and its isotopes. To store hydrogen is to store energy. The storage capacity of a metal/ alloy is determined mainly by the diffusion parameters namely the pre-exponential factor of diffusion constant and the activation energy. Not much work is done regarding diffusion parameters of hydrogen isotopes in Mg_2Ni except the ab-initio calculation and green's function approach. Hence in this theoretical investigation, the diffusion parameters of hydrogen isotopes in Mg_2Ni are computed using a reaction coordinate approach incorporating a scattering matrix formalism and green function technique. Our results are compared with the existing theoretical results.

Keywords: Mg_2Ni, eigen values, eigen vectors, mean square displacement, diffusion parameters, hydrogen isotopes, green function techniques, scattering matrix formalism and reaction coordinates.

1. Introduction

Hydrogen energy is a kind of high efficient and clean secondary energy. Hydrogen storage plays a vital role in both hydrogen production and hydrogen applications. The important properties of the hydrogen storage materials in automotive applications are (i) light weight, (ii) cost and availability, (iii) high volumetric and gravimetric density of hydrogen, (iv) fast kinetics, (v) ease of activation, (vi) low temperature of dissociation or decomposition, (vii) appropriate thermodynamic properties, (viii) long-term cycling stability, and (ix) high degree of reversibility [1-3].

Recently, many researchers have focused their attention towards exploring Mg and Mg based alloys for hydrogen storage. The Mg-based metallic hydrides have low specific weight, low cost and high hydrogen capacity for e.g. 7.6 wt.% for MgH_2, 3.6 wt.% for Mg_2NiH_4 [4]. In order to use metal hydrides as energy carriers in mobile vehicles, the total mass of the storage system needs to be reduced. The metallic Mg has hexagonal crystal structure. After absorption of hydrogen Mg_2NiH_4 has become cubic antiflurite structure [5]. By calculation, the bond length of Mg_2NiH_4 is d_{Ni-H}= 1.548 Å while the experimental value is 1.55 Å [6]. The electronic bond structure of this compound with regular tetrahedral arrangement produces a semiconductor with an indirect gap of 1.17 eV. It is conformed that hydrogen is covalently bonded with nickel forming a complex $[NiH_4]^{4-}$ which in turn bonds ionically to the Mg^{2+} ions in Mg_2NiH_4 by the calculated charge distribution [7]. Not much work is done regarding diffusion parameters except the ab initio calculation and green's function approach [2,5]. In this paper the estimated results of diffusion parameters of hydrogen isotopes $_1H^1$, $_1H^2$ and $_1H^3$ in Mg_2Ni using reaction coordinate incorporating

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green's function technique and scattering formalism are reported.

2. Method of calculation

In this lattice dynamical investigation, the first step is to compute the phonon frequencies and eigen vectors of the host material Mg_2Ni. The phonon frequencies and eigen vectors of Mg_2Ni are estimated using Born-von Karman formalism considering interactions up to three neighbors.

The force constant values in the dynamical matrix are estimated using the Morse potential with parameters [8,9] and are listed in Table 1.

The dynamical matrix thus obtained is a (9 × 9) Hermitian matrix. It has been converted into a real symmetric matrix of the order (18 × 18). Diagonalization of this matrix yields the phonon frequencies and polarization vectors.

Table 1. Force constant values in 10^4 dynes/cm

Parameter	A_{11}	B_{11}	A_{12}	B_{12}	C_{12}	A_{13}
Value	0.9123	0.022	-0.0291	-0.0291	0.0654	-0.0667
Parameter	B_{13}	A_{21}	B_{21}	A_{22}	B_{22}	C_{22}
Value	0.014	0.5682	0.5682	-0.0619	-0.0249	0.0044
Parameter	D_{22}	A_{23}	B_{23}	C_{23}	D_{23}	A_{31}
value	0.0044	-0.0045	-0.0045	-0.0019	0.00065	0.9123
Parameter	B_{31}	A_{32}	B_{32}	C_{32}	A_{33}	B_{33}
value	0.022	-0.291	0.0291	0.0654	-0.0171	-0.0171
Parameter	A_{51}	B_{51}	C_{51}	A_{52}	B_{52}	A_{53}
value	0.8827	0.8827	0.0485	-0.1388	0.016	-0.0016
Parameter	B_{53}	C_{53}	A_{61}	B_{61}	A_{62}	B_{62}
value	-0.0016	0.00026	0.5682	0.5682	-0.0619	-0.0249
Parameter	C_{62}	D_{62}	A_{63}	B_{63}	C_{63}	D_{63}
value	0.0044	0.0044	-0.0045	-0.0045	-0.0019	0.00065

Using the phonon frequencies and eigen vectors, the Green's function values are calculated by using the equation [10],

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

where ω_{max} is the maximum frequency among all normal modes of the host crystal. Using eigen values and eigen vectors, the green's function values have been evaluated which in turn are used to calculate the diffusion parameters.

The defect modes are obtained by solving the secular equation

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

where I is the Unit matrix, g is the Green's function matrix, δl in 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 displacement of the four neighboring metal atoms surrounding the interstitial hydrogen is obtained using the equation,

$$u_1 = \left\{ I + g(\delta l + a\gamma a^T)\left[I - g(\delta l + a\gamma a^T)\right]^{-1} \right\} u_\alpha \ldots (3)$$

with u_α as

$$u_\alpha\begin{pmatrix} l \\ k ;\vec{q}j \end{pmatrix} = \left\{ \frac{1}{2Nm_k\omega_{qj}} \right\} e_\alpha(\kappa,\vec{q}j) \exp\left[i\vec{q}.r\begin{pmatrix} l \\ k \end{pmatrix} \right] \quad \ldots (4)$$

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

The displacement of hydrogen isotope is computed using the equation

$$\xi = -\gamma a^T u_1 \quad \ldots (5)$$

In the jumping 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 phonons created by lattice vibrations.

The reaction coordinate is estimated using the equation

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$$\chi = \left(\xi_d - \frac{1}{m} \sum_j \bar{u}_j \right) . \xi \qquad \ldots (6)$$

where ξ_d and u_j are displacements of diffusing atom and host atoms respectively.

Using the reaction coordinates the jump frequency is computed using the equation

$$\Gamma = \left[\frac{\Sigma_{q,j} \omega^2(q,j) |\chi(q,j)|^2}{\Sigma_{q,j} |\chi(q,j)|^2} \right] \times \exp\left[-\frac{\chi_c^2}{\Sigma_{q,j} |\chi(q,j)|^2} \right] \qquad \ldots (7)$$

From this equation, Γ_0 is identified as

$$\Gamma_0 = \left[\frac{\Sigma_{q,j} \omega^2(q,j) |\chi(q,j)|^2}{\Sigma_{q,j} |\chi(q,j)|^2} \right]^{\frac{1}{2}}$$

the activation energy E_a is calculated using the golden rule.

$$\Gamma = \Gamma_0 \exp\left(-\frac{E_a}{k_B T} \right) \qquad \ldots (8)$$

The pre exponential factor of diffusion D_0 is calculated by

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

3. Results and Discussion

a) Phonon frequencies and eigen vectors

The phonon frequencies and eigen vectors have been calculated for a set of 122 wave vector points obtained by uniformly dividing the Brillouin zone [11,12].

b) Mean Square Displacement

The displacement of nearby host atoms changes due to the presence of interstitial hydrogen. The mean square displacement values for different temperatures are estimated and are compared with defect free material as shown in fig. 1. MSD values is increases with temperature as expected. More over the MSD of atoms surrounding H defect, D defect and T defect is decreased effectively. This is because of the creation of resonance modes. During the resonance nodes of vibration, the vibrational amplitude of hydrogen isotopes are expected to be huge with the expense of that of the neighboring atoms.

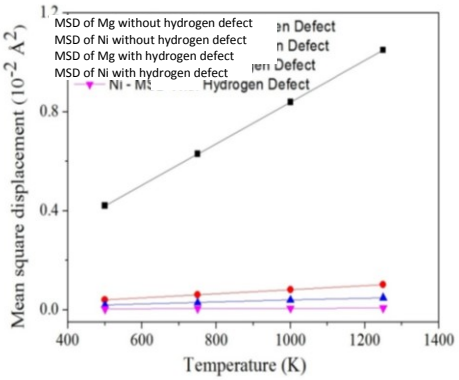

Figure 1(a). Mean square displacement of atoms surrounding the H-defect

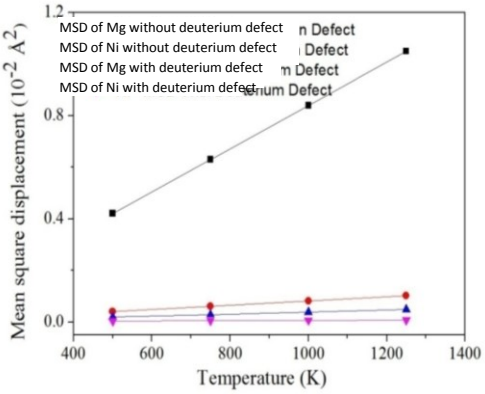

Figure 1(b). Mean square displacement of atoms surrounding the D-defect

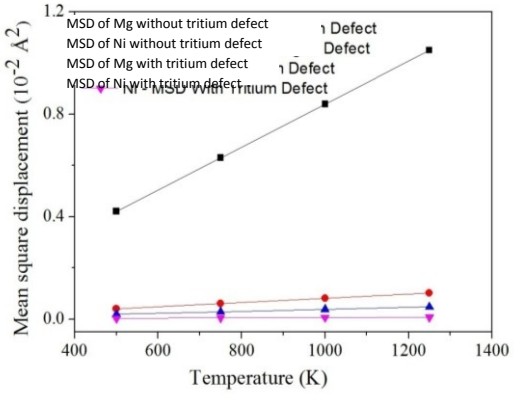

Figure 1(c). Mean square displacement of atoms surrounding the T-defect

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c) Jump frequency values

Using green's function values and the reshape in dynamical matrix due to the presence of hydrogen and their isotopes (H, D and T) the jump frequency values were estimated using reaction coordinate technique at different temperatures and these values are given in table 2.

Table 2. Jump frequency values at different temperature

Isotopes	Temperature (K)	Jump frequency Γ sec^{-1}
hydrogen	500	2.80E+07
	750	2.35E+09
	1000	2.16E+10
	1250	8.17E+10
deuterium	500	1.57E+07
	750	1.59E+09
	1000	1.60E+10
	1250	6.43E+10
tritium	500	8.72E+06
	750	1.09E+09
	1000	1.22E+10
	1250	5.21E+10

d) Diffusion parameters

The lnΓ 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 Γ_0 and activation energy values are determined. The D_0 value was calculated using the Eqn.

$$D_0 = \frac{\Gamma_0 l^2}{6} \qquad \ldots (9)$$

which is found be $D_0 = 2.84615 \times 10^{-8}$ m^2 sec^{-1} for hydrogen. E_a calculated from the slope is found to be 0.564 eV. Our calculated results are compared with that computed employing Quasielastic neutron scattering and NMR studies [13] in table 3. Our result is found to be comparable with the experimental results. The activation energy increases with isotopic mass. This is a welcome trend. Moreover the activation energy for hydrogen diffusion is found to be 0.564 eV, which is low. Hence hydrogen can easily diffuse and occupy the interstitical positions. Moreover the stored hydrogen can easily be retrieved for end use.

Table 3. Diffusion parameters of H in Mg_2Ni

Diffusing Atom	Pre-exponential factor D_0 (10^{-8} m^2 sec^{-1})	Activation energy E_a (meV)	Reference
H	2.84615	564	This study
D	2.84428	594	
T	2.84895	615	
H	1.084	563.8	[13]

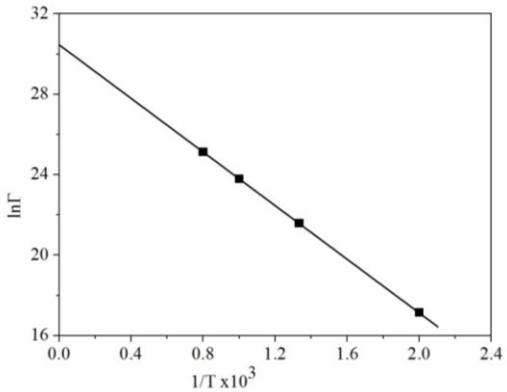

Figure 2(a). Logarithm of Jump frequency vs. 1/T for Hydrogen in Mg_2Ni

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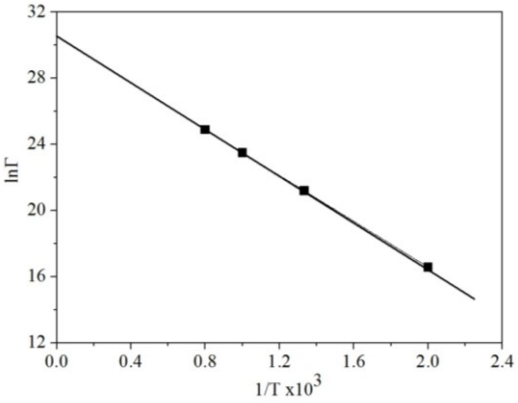

Figure 2(b). Logarithm of Jump frequency vs. 1/T for Deuterium in Mg_2Ni

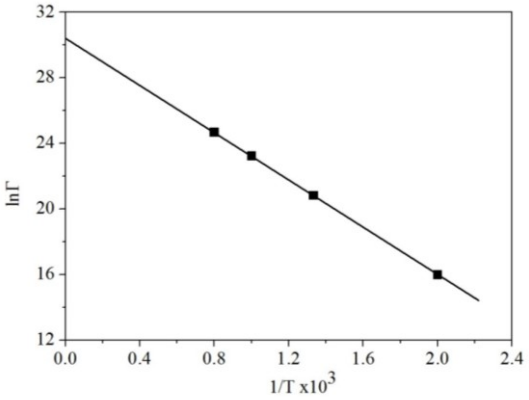

Figure 2(c). Logarithm of Jump frequency vs. 1/T for Tritium in Mg_2Ni

A comparative study is made as shown in table 4.

Table 4. Comparative study

Temperature (K)	D_H	D_D	D_T	Ratio D_D / D_H	Ratio D_T / D_H
500	5.81187 E-14	3.1981E-14	2.01346 E-14	0.550271	0.346439
750	4.58E-12	3.07552 E-12	2.26042 E-12	0.67	0.49
1000	4.06711 E-11	3.016E-11	2.39504 E-11	0.741559	0.58888
1250	1.50758 E-10	1.1867E-10	0.98716 E-10	0.787153	0.654798

From the last two columns it is concluded, D_D/D_H and D_T/D_H values are found to be less than one as expected. This result is in support of usage of this alloy for the application towards hydrogen isotope separation.

4. Conclusion

The eigen values and eigen functions of the cubic Laves phased compound Mg_2Ni are estimated by Born-von Karman formalism. The localized vibrational modes have been used to worked out with hydrogen atoms as an interstitial defect in this system. A green's function technique and the scattering matrix formalism are used to calculated the MSD values of Hydrogen isotopes (H, D and T) and its neighbors at 500, 750, 1000 and 1250 K temperatures. A reaction coordinate technique has been used to compute the diffusion parameters of Hydrogen isotopes (H, D and T) in Mg_2Ni. These values are found to be in good agreement with the existing experimental result.

5. References

[1] Haussermann, U., Blomqvist, H. and Noréus, D., "Bonding and Stability of the Hydrogen Storage Material Mg_2NiH_4". Inorganic Chemistry, 41, 2002, 3684-3692. http://dx.doi.org/10.1021/ic0201046.

[2] Van Setten, M.J., De Wijs, G.A. and Brocks, G., "Ab Initio Study of the Effects of Transition Metal Doping of Mg_2NiH_4". Physical Review B, 76, 2007, Article ID: 075125. http://dx.doi.org/10.1103/PhysRevB.76.075125

[3] Jezierski, A., Jurczyk, M. and Szajek, A., "Electronic Structure of $Mg_2Ni_{1-x}Cu_x$". Actaphysicapolonica A, 115, 2009, 223-225.

[4] Zhang Yanghuan, Yang Tai, Shang Hongwei, Zhang Guofang, CAI Ying, Zhao Dongliang, Gaseous and

Electrochemical Hydrogen Storage Kinetics of As-quenched Nanocrystalline and Amorphous, Mg_2Ni-type Alloys, 604, Vol.28, No.3, ZHANG Yanghuan et al. Gaseous and Electrochemical Hydrogen Storage.

[5] Antony, M., Lawrence, N. and Rayappan, J.B., J. Comput. Theor. Nanosci. 12, 2015, 413-417.

[6] Garcia, G.N., Abriata, J.P. and Sofo, J.O., Phys. Rev. B 59, 1999, 746.

[7] Wang, S.P., Guo, J.G. and Jiang, Y., J. Comput. Theor. Nanosci. 10, 2013, 250.

[8] Rui Yu, Pengcheng Zhai, Guodong Li and Lisheng Liu, J. Elect. Materials 41, 2012, 1465.

[9] Girifalcom, L.A. and Weizer, V.G., Phys. Rev. 114, 1959, 687.

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

[11] Balaguru, R.J.B., Lawrence, N. and Raj, S.A.C., Int. J. Mod. Phys. B 16, 2002, 4111.

[12] Disalvo, F.J., Moncton, D.E. and Waszczak, J.V., Phys. Rev. B 14, 1976, 4321.

[13] Cermak, J. and Kral, L., Acta Materialia 56, 2008, 2677.