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Lattice Dynamical Investigation of Hydrogen Energy Storage in Metallic Alloys

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Abstract : Hydrogen is the promising medium for both energy transmission and storage. Hydrogen can be stored safely inside certain metals and alloys. Attempts have been made for selecting good energy storage media. In the present work, the diffusion of hydrogen and deuterium in the bcc substitutional alloy Cr_{0.7}Fe_{0.3} and fcc substitutional alloy Ni_{0.5}Fe_{0.5} have been reported in which Born-von Karman formalism with average atomic mass is used to compute the phonon dispersion. Mean Square Displacements (MSD) with hydrogen and deuterium interstitials are calculated for the temperature range 500K-1250K with normal to 2.5GPa pressure by applying Green's function technique and scattering matrix formalism. The diffusion parameters are calculated using reaction coordinate technique in which the diffusivity is characterized by the diffusion constant $D = D_0 \exp(-E_a/k_B T)$ which determines the storage capacity of the given systems of study. The diffusion parameters obtained for Ni_{0.5}Fe_{0.5} at normal pressure is D (cm²/s) = $7.6244 \times 10^{-3} \exp(-92.4827 \text{ meV}/k_B T)$ whereas for Cr_{0.7}Fe_{0.3} at normal pressure is D (cm²/s) = $4.327440 \times 10^{-5} \exp(-128.658 \text{ meV}/k_B T)$. On comparison, it is observed that the activation energy in Ni_{0.5}Fe_{0.5} is very much less than that in Cr_{0.7}Fe_{0.3} and other experimental reported systems like Fe_{0.5}Ti_{0.5} and Cr-Fe. It is observed that the diffusivity of Cr_{0.7}Fe_{0.3} is 1000 times greater than that of Cr-Fe system for a given temperature. A gradual decrease of diffusivity with increase in pressure indicates that Cr_{0.7}Fe_{0.3} should be maintained at constant pressure while using it as storage medium. Also the variation of diffusion parameter with pressure in Ni_{0.5}Fe_{0.5} indicates that the pressure does not influence much on the diffusion of hydrogen isotopes.

Keywords: diffusion, hydrogen energy storage, activation energy, metallic alloys.

1. Introduction

The mechanism of diffusion of hydrogen in metals and alloys used to be one of the biggest unsolved problems of diffusion in solids. Hydrogen can be stored safely inside certain metals and alloys and is the promising medium for both energy transmission and storage. Attempts have been made for selecting good energy storage media. With a variety of experimental data on the nature of hydrogen diffusion in metals from absorption / desorption, NMR, Gorsky, Neutron scattering, etc., a wide range of values for the diffusion parameters have emerged. So a proper understanding of the diffusion parameters is essential to select a better metal or alloy to store hydrogen. Several calculations have been published on the activation energy for impurity diffusion in metals. The bcc and fcc metals have been a center of interest for several years. Most of the theoretical studies dealing with the diffusion of hydrogen in metals are formulated on the basis of small polaron theory developed by Holstein¹.

In the present work, the diffusion of hydrogen and deuterium in the *bcc* substitutional alloy Cr_{0.7}Fe_{0.3} and *bcc* substitutional alloy Ni_{0.5}Fe_{0.5} have been reported. Since the effects of force constants and mass disorder are small for these disordered alloys, Born-von Karman formalism using the average atomic mass and resulting in average force constants, can be used to compute the phonon dispersion[2]. When H / ²H is pumped into this alloy, it migrates through the host lattices by thermally activated jump to neighbouring empty interstitial sites. In the higher temperature limit, both octahedral(O) and tetrahedral(d) sites are occupied with the interstitial atoms and both (O-O) and (d-d) jumps are possible. Earlier studies[3] revealed that the results for both jump mechanisms are of same order. Hence, only (O-O) jump mechanism is considered in the present study. Mean Square Displacements (MSD) with hydrogen and deuterium interstitials are calculated for the temperature range 500K-1250K with normal to 2.5GPa pressure by applying Green's function technique and scattering matrix formalism. The diffusivity is characterized by the diffusion constant $D = D_0 \exp(-E_a / k_b T)$ which determines the storage capacity of the given system of study.

2. Method of calculation

The substitutional alloy Cr_{0.7}Fe_{0.3} has the lattice constant $a_0 = 2.877 \text{ \AA}$ and Ni_{0.5}Fe_{0.5} has the lattice constant $a_0 = 3.5868 \text{ \AA}$ at NTP. The phonon frequencies of the normal modes of vibration are calculated by solving the secular equation

$$|D(q) - \omega^2 I| = 0 \tag{1}$$

where D , the dynamical matrix is given by

$$D \begin{pmatrix} q & \\ k & k' \end{pmatrix} = \frac{1}{\sqrt{m_k m_{k'}}} \sum_{l, l'} \Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ k & k' \end{pmatrix} \exp(iq \cdot (R(l) - R(l'))) \tag{2}$$

Here, $\Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ k & k' \end{pmatrix}$ is the atomic force constant, $R(l)$ and $R(l')$ are the position vectors, q is the wave vector, m_k is the mass of k -th atom and $m_{k'}$ is the mass of the k' -th atom in the l -th and l' -th unit cells, respectively. A Born-von Karman formalism considering interactions upto sixth nearest neighbours is used to work out the dynamical matrix for Cr_{0.7}Fe_{0.3} alloy. The matrix diagonalization is carried out for 73 wave vector points of the *bcc* lattice. Similarly the dynamical matrix elements are evaluated by extending to fifth neighbour interaction and the matrix diagonalization is carried out for 73 wave vector points of the *fcc* lattice of Ni_{0.5}Fe_{0.5}. The force constant parameters used for the calculation of phonon dispersion are arranged in Table.1 and Table.2.

For Cr_{0.7}Fe_{0.3} alloy, with hydrogen in one of the octahedral position $(0 \ 0 \ 0)_{a_0}$, there are two nearest neighbour metal atoms at $(0 \ \frac{1}{2} \ 0)_{a_0}$ and $(0 \ \bar{\frac{1}{2}} \ 0)_{a_0}$ positions and four next nearest neighbour metals at the positions $(\frac{\sqrt{2}}{2} \ \frac{1}{2} \ 0)_{a_0}$, $(\frac{\sqrt{2}}{2} \ \frac{1}{2} \ 0)_{a_0}$, $(\frac{\sqrt{2}}{2} \ \bar{\frac{1}{2}} \ 0)_{a_0}$, and $(\frac{\sqrt{2}}{2} \ \bar{\frac{1}{2}} \ 0)_{a_0}$. Also for the alloy Ni_{0.5}Fe_{0.5}, hydrogen occupies the octahedral interstitial site. With the interstitial atom in the $(0 \ 0 \ 0)_{a_0}$ position, there are six nearest neighbour metal atoms at the positions $(\frac{\sqrt{2}}{2} \ 0 \ 0)_{a_0}$, $(\frac{\sqrt{2}}{2} \ 0 \ 0)_{a_0}$, $(\frac{1}{2} \ 0 \ 0)_{a_0}$, $(\bar{\frac{1}{2}} \ 0 \ 0)_{a_0}$, $(0 \ \frac{1}{2} \ 0)_{a_0}$ and $(0 \ 0 \ \frac{1}{2})_{a_0}$.

Table 1. Force constant parameters of Cr_{0.7}Fe_{0.3} alloy for normal pressure

Position of atoms (a_0)	Force constant parameters	Force Constant Value (N/m)	Position of atoms (a_0)	Force constant parameters	Force Constant Value (N/m)
$\begin{pmatrix} 1 & 1 & 1 \\ 2 & 2 & 2 \end{pmatrix}$	A1	12.013	$\begin{pmatrix} 3 & 1 & 1 \\ 2 & 2 & 2 \end{pmatrix}$	A4	-0.135
	B1	12.553		B4	-0.1291
$\langle 00 \rangle$	A2	20.980		C4	-0.389

	B2	-0.170		D4	-1.171
$\langle 10 \rangle$	A3	0.940	$\langle 11 \rangle$	A5	2.973
	B3	0.470		B5	2.083
	C3	0.470	$\langle 00 \rangle$	A6	3.430
				B6	-1.840

Table 2. Force constant parameters of Ni_{0.5}Fe_{0.5} alloy at normal pressure

Position of atoms (a ₀)	Force constant parameters	Force Constant Value (N/m)	Position of atoms (a ₀)	Force constant parameters	Force Constant Value (N/m)
$\begin{pmatrix} 1 & 1 \\ 2 & 2 \end{pmatrix} 0$	A ₁	16.4800	$\langle 10 \rangle$	A ₄	0.4900
	B ₁	18.7200		B ₄	0.4700
	C ₁	-1.2900		C ₄	-0.4100
$\langle 00 \rangle$	A ₂	0.4500	$\begin{pmatrix} 3 & 1 \\ 2 & 2 \end{pmatrix} 0$	A ₅	-0.3300
	B ₂	-0.0400		B ₅	-0.1400
$\begin{pmatrix} 1 & 1 & 1 \\ 2 & 2 & 2 \end{pmatrix}$	A ₃	0.5700		C ₅	0.0400
	B ₃	0.3000		D ₅	0.0800
	C ₃	0.1500			
	D ₃	0.1900			

The displacement of the six metal atoms in the defect space are calculated for both alloys using the relation

$$U_1 = \left[I + g \left| \delta l + a \gamma a^T \right| \left| I - g \left| \delta l + a \gamma a^T \right| \right|^{-1} \right] U_{10} \tag{3}$$

and the (18x18) Green’s function matrix *g* of the metal atoms is calculated from the equation

$$g_{\alpha\beta} \begin{pmatrix} 0 & l \\ k & k' \end{pmatrix} = \frac{1}{N \sqrt{m_k m_{k'}}} \sum_{q,j} \frac{e_\alpha |k| q j \rangle e_\beta^* |k'| q j \rangle}{\left| \omega_{\max}^2 - \omega_j^2 \right| |q|} \exp \left[2\pi i |q \cdot r| k k' \right] \tag{4}$$

where *N* is the total number of cells in the unperturbed crystal, *e_α |k|qj* is the α-th component of the eigen vectors of the phonon $|q, j\rangle$, *r* defines the distance of the *k'*-th atom in the *l*-th cell from the *k*-th atom in the zeroth cell (reference cell) and ω_{\max} is the maximum angular frequency of the host crystal. The change in the dynamical matrix δl of order (18x18) is calculated from Morse potential and the elements of metal-hydrogen interaction matrix *a* of order (18 x 3) are fitted with a potential form $\phi = -\alpha/r^4 + \beta/r^8$ discussed by Machlin[4].

The (3 x 3) interstitial Green’s function matrix γ is defined as

$$\gamma \langle \mathbf{e}^2 \rangle = \left[m_s \langle \mathbf{e}_j^2 \rangle - \omega_l^2 \right] I \tag{5}$$

where *m_s* is the mass of the interstitial atom and ω_l is the vibrational frequency of the interstitial in the

otherwise frozen lattice. The γ matrix is found to be of the form $\begin{bmatrix} \gamma_1 & 0 & 0 \\ 0 & \gamma_1 & 0 \\ 0 & 0 & \gamma_2 \end{bmatrix}$. The matrix *U₁₀* of order (18 x

1) represents the displacement of the six host crystal atoms in the normal lattice. The displacement of the interstitial hydrogen atom is calculated using the relation

$$\xi = -\gamma a^T U_1. \tag{6}$$

Since U_1 involves the inverse matrix which is complex in nature and is of the order (18 x 18), more computer time is needed. In order to reduce this time, g and \mathcal{D} matrices are block diagonalized using the symmetric coordinates for the D_{4h} group. The mean square displacement values are calculated using the relation

$$\langle U_1^2 | q, \omega \rangle = \frac{1}{2} \int_0^\infty \frac{U^2 | q, \omega |}{\omega} \coth\left(\frac{\hbar\omega}{2k_B T}\right) d\omega, \quad (7)$$

and the diffusion coefficients of hydrogen in the alloy are calculated by applying reaction coordinate approach suggested by Flynn⁵ in the limit of an elastic continuum. When hydrogen jumps from one interstitial position to other, the neighbours exert a strong repulsive force on jumping atoms when they approach the saddle point. The jump will be completed only if the fluctuations in the reaction coordinate of diffusing atom are sufficiently strong to force the moving atom past its neighbours towards the vacant position. The reaction coordinate is defined as

$$\chi | q, j \rangle = \left[\xi_d - \left(\frac{1}{m'}\right) \sum_{q,j} U_j \right] \cdot \hat{\chi} \quad \text{with } j = 1, 2, 3, \dots, m', \quad (8)$$

where ξ_d is the displacement of diffusing atom and U_j is the displacement of the j -th atom of m' neighbouring atoms obstructing the jump. The jump occurs when the coordinate χ exceeds a critical value called χ_c which is considered as 30% of the atomic radius of the metal atoms. The jump frequency of hydrogen has been obtained from the equation

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

Hence the diffusion coefficient at a given temperature T is calculated using the equation

$$D = D_0 \exp \left(-E_a / k_B T \right), \quad (10)$$

where E_a is the activation energy and D_0 is the pre-exponential factor estimated from the relation

$$D_0 = \frac{\Gamma_0 l^2}{6} \quad (11)$$

with Γ_0 and l are respectively, the pre-exponential factor of the jump frequency and jump distance. When the pressure is increased, the lattice gets compressed. The new lattice parameters are calculated using the compressibility relation.

3. Results and discussion

The calculated phonon frequencies of the $\text{Cr}_{0.7}\text{Fe}_{0.3}$ system using Born-von Karman model are shown in Figure 1 along with the existing experimental results⁶ measured using the neutron inelastic scattering for normal pressure. A good agreement with the experimental result shows that the Born-von Karman formalism using a sixth nearest neighbour force constant *bcc* model considering averaged atomic mass, provides a satisfactory fit to the phonon dispersion curves of this alloy. The phonon frequency distribution for the *bcc* model was also calculated.

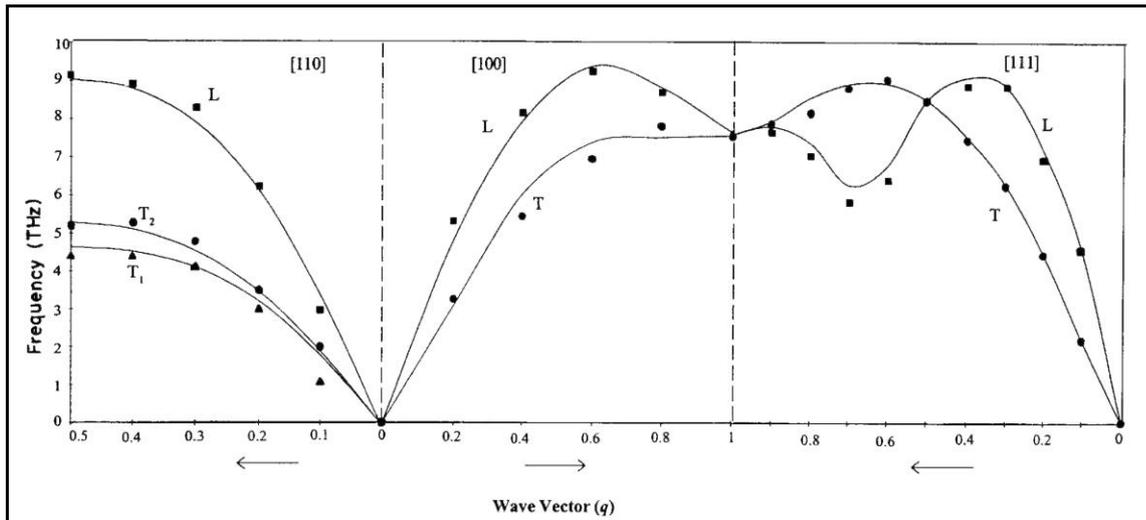


Figure 1. Phonon dispersion in $\text{Cr}_{0.7}\text{Fe}_{0.3}$ alloy. The solid curves represent the theoretical curves obtained in the present work. ▲ ■ • Experimental data of Lloyd et al.

Similarly the evaluated phonon frequency dispersion for $\text{Ni}_{0.5}\text{Fe}_{0.5}$ at normal pressure is shown in Figure 2 along with the inelastic slow neutron diffraction experimental data² and another theoretical result carried out in the frame work of transition metal-model potential approach by Okoye and Satya Pal[7]. It is found that the computed values agree well with the experimental values whereas the values obtained by Okoye and Satya Pal[7] fall short of the experimental data. Thus, a Born-von Karman analysis using the average atomic mass and resulting average force constants is justified for this alloy. At high pressures, the lattice parameters are decreased due to reduction in volume. With the new lattice constant values, phonon frequencies are determined and they are found to be increased with pressure as expected.

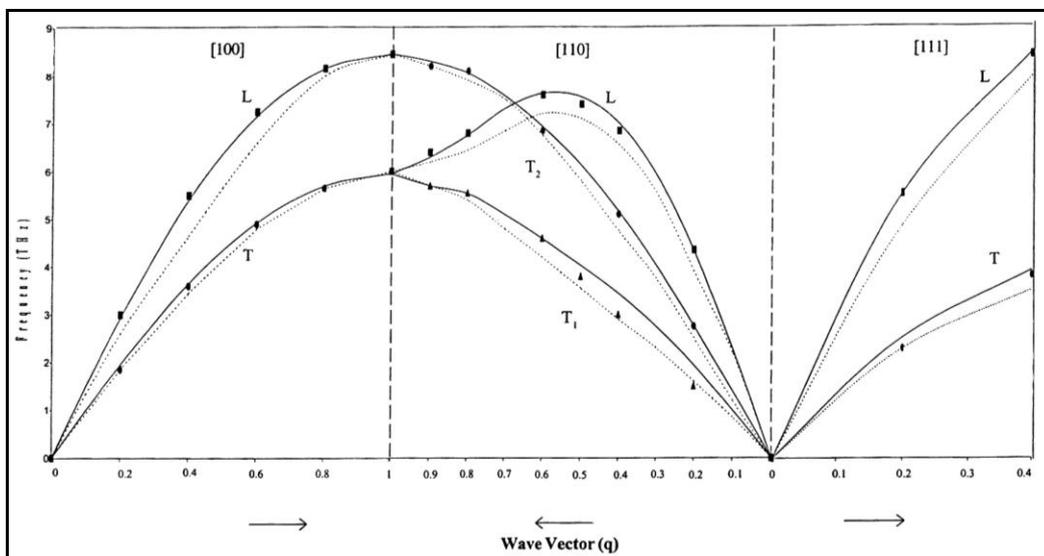


Figure 2 Phonon dispersion in $\text{Ni}_{0.5}\text{Fe}_{0.5}$ alloy. — Theoretical curves obtained in the present work. Theoretical curves obtained by Okoye and Satya Pal. ▲ ■ • Experimental data of Hallman and Brockhouse

The H / ^2H interstitial atom occupies the octahedral positions of the $\text{Cr}_{0.7}\text{Fe}_{0.3}$ bcc lattice and the metal atoms close to it relax from their equilibrium positions due to the coupling between the interstice and metal atoms. With the help of the evaluated Green's function values, the MSD of defect space atoms are calculated for the temperatures 500K, 750 K, 1000K and 1250K. The variation of MSD values with temperature for H and ^2H interstitial are shown in Figures 3 and 4, respectively. It is found that the MSD values increase with the temperature as expected. The MSD values of defect space atoms are greatly reduced from that of host crystal values because the metal atoms in defect space vibrate in a potential which differ much from that of host crystal due to the change in coupling constants between the atoms in the defect space. Also due to the lighter nature of

hydrogen whose vibrational amplitude is very large, smaller MSD values of surrounding atoms have been obtained.

Also the MSD of the defect space atoms of $Ni_{0.5}Fe_{0.5}$ are calculated. Moreover, the MSD of defect space atoms are found to be less than that of host crystal. This is attributed to the coupled vibrational motion of interstitial H with surrounding metal atoms. The same trend has been observed experimentally for the NbH_x system[8-10]. The variation of MSD values with temperature for H and 2H interstitial under normal pressure are shown in Figures 5 and 6 respectively.

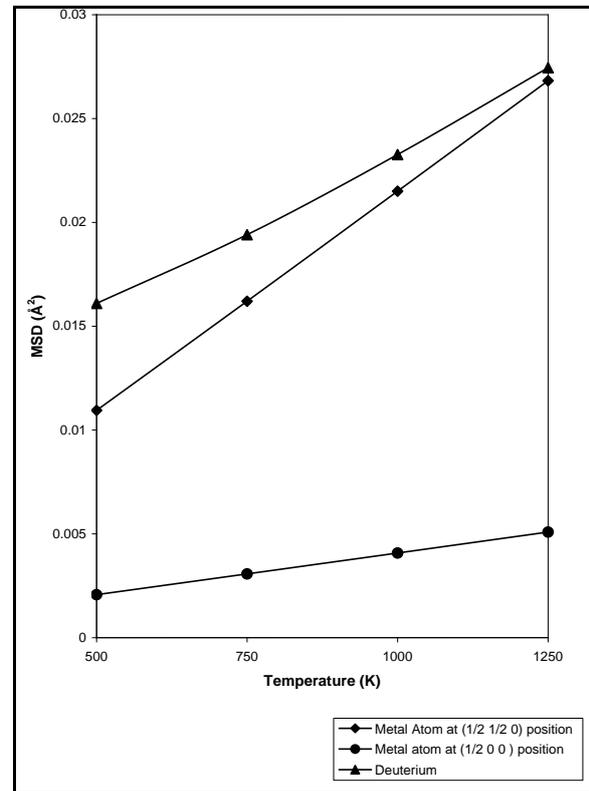
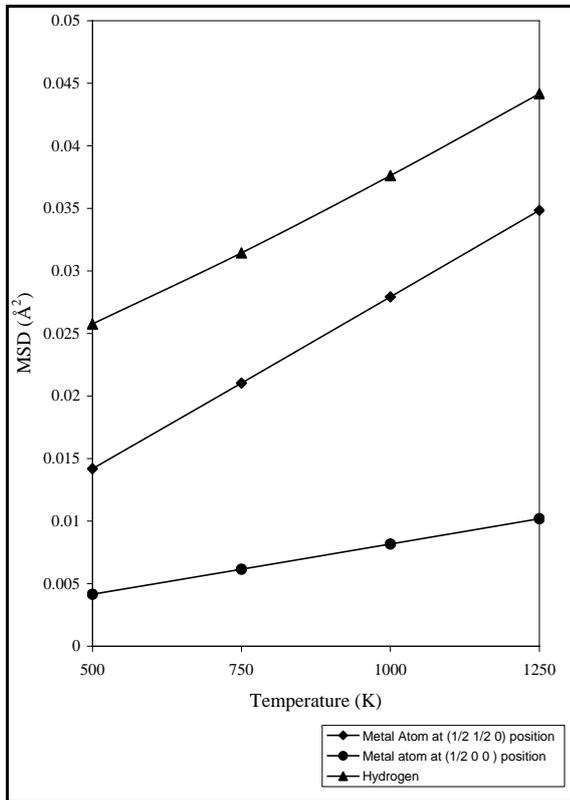


Figure 3. MSD of $Cr_{0.7}Fe_{0.3}$ with hydrogen interstitial Figure 4. MSD of $Cr_{0.7}Fe_{0.3}$ with deuterium interstitial

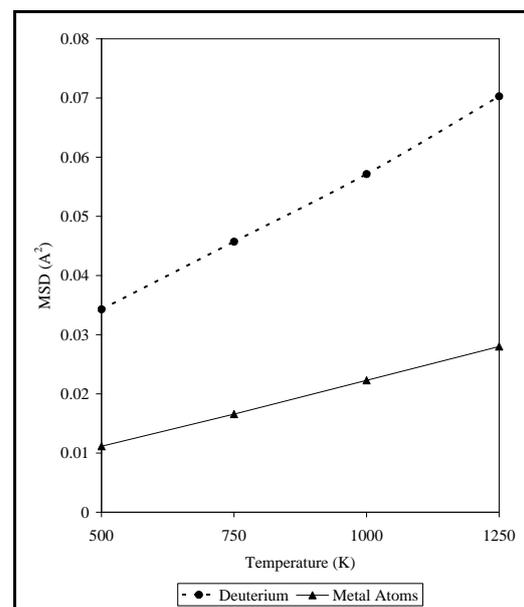
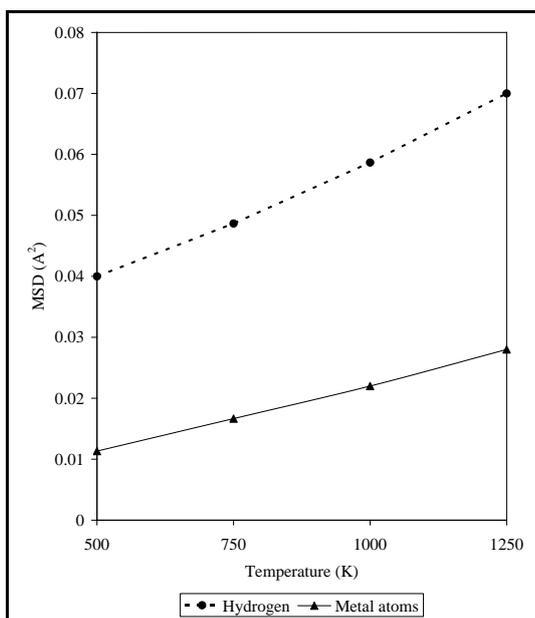


Figure 5. MSD of $Ni_{0.5}Fe_{0.5}$ with hydrogen interstitial Figure 6. MSD of $Ni_{0.5}Fe_{0.5}$ with deuterium interstitial

The value of diffusion parameters obtained for $\text{Cr}_{0.7}\text{Fe}_{0.3}$ at normal pressure is given below:

For Hydrogen, $D \text{ (cm}^2\text{/s)} = 4.327440 \times 10^{-5} \exp(-128.658 \text{ meV}/k_B T)$

For Deuterium, $D \text{ (cm}^2\text{/s)} = 4.220923 \times 10^{-5} \exp(-249.727 \text{ meV}/k_B T)$

For a given temperature and pressure, it is found that the diffusion coefficient for ^2H is less than that of H. The results are compared with the reported experimental diffusion parameters of H in $\text{Cr}_{0.5}\text{Fe}_{0.5}$ alloy[11] given as $D \text{ (cm}^2\text{/s)} = 1.80 \times 10^{-5} \exp(-351.344 \text{ meV}/k_B T)$. It is observed that the diffusivity of $\text{Cr}_{0.7}\text{Fe}_{0.3}$ is 1000 times greater than that of $\text{Cr}_{0.5}\text{Fe}_{0.5}$ system for a given temperature. In $\text{Cr}_{0.7}\text{Fe}_{0.3}$ system, hydrogen diffuses faster than deuterium in the temperature region investigated. The pre-exponential factor is almost independent of isotopes whereas for the activation energy, the relation $E_{a,H} < E_{a,^2H}$ holds good. The isotope effect is similar to what was observed for diffusion of H in *bcc* metals like Nb and V. In the low temperature region, the diffusivity ratio $D_H/D_{^2H}$ increases abruptly to the value of 18 and as reported earlier for some *bcc* metals[12], it approaches the value of $\sqrt{2}$ gradually in the high temperature region. Also the diffusivity ratio $D_H/D_{^2H}$ is always greater than unity and it is temperature and pressure dependent as already mentioned by Alefeld and Volkl[13]. When the pressure increases, the diffusivity decreases slightly. The variation of diffusivity D with pressure at the temperature of 500 K is shown in Figure 7. A gradual decrease of diffusivity with increase in pressure indicates that the present system of study $\text{Cr}_{0.7}\text{Fe}_{0.3}$ should be maintained at constant pressure while using it as storage medium.

The diffusion constants of $\text{Ni}_{0.5}\text{Fe}_{0.5}$ obtained for normal pressure is given below:

For H, $D \text{ (cm}^2\text{/s)} = 7.6244 \times 10^{-3} \exp(-92.4827 \text{ meV} / k_B T)$.

For ^2H , $D \text{ (cm}^2\text{/s)} = 6.5800 \times 10^{-3} \exp(-137.1372 \text{ meV} / k_B T)$.

It is found that the activation energy for deuterium is greater than that of for hydrogen. Arrhenius behaviour is observed over the complete temperature range of study. It is observed that the pre-exponential factor D_0 is mass dependent and obeys the law $\frac{D_0^H}{D_0^{^2H}} = \sqrt{\frac{m_{^2H}}{m_H}}$ within error bars. Previous result[14] states that below certain temperature (773K for Pd), *fcc* metals show the reverse isotope dependence on the activation energy. But the $\text{Ni}_{0.5}\text{Fe}_{0.5}$ system shows the normal isotope effect $E_{a,H} < E_{a,^2H}$ at the temperature range of study. The diffusivity ratio $D_H/D_{^2H}$ is always greater than 1 and approaches the value of 1.75 at higher temperature. This is due to the high activation energy of deuterium. Also the variation of diffusion parameter with pressure in $\text{Ni}_{0.5}\text{Fe}_{0.5}$ at the temperature of 500K is shown in Figure 8.

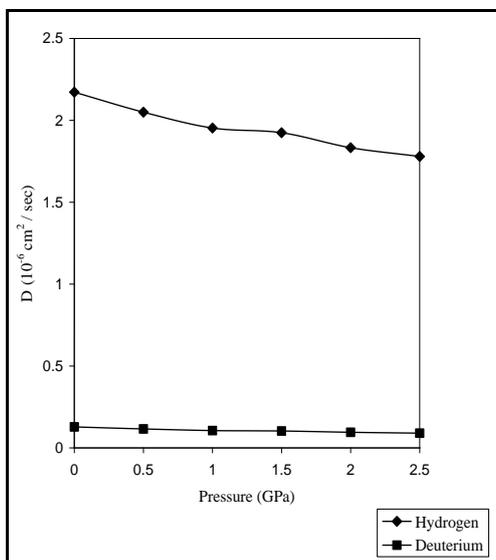


Figure 7. Diffusivity of H and ^2H in $\text{Cr}_{0.7}\text{Fe}_{0.3}$ as a function of pressure

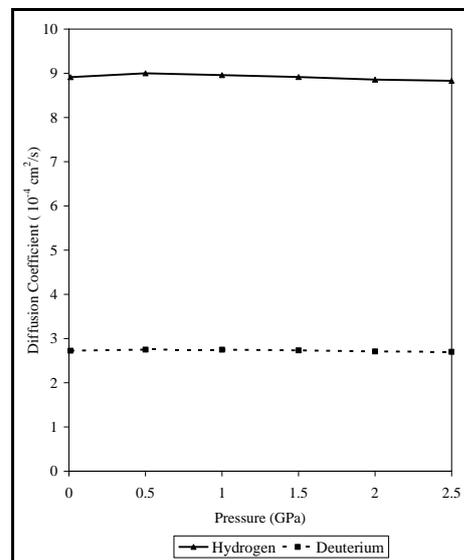


Figure 8. Diffusivity of H and ^2H in $\text{Ni}_{0.5}\text{Fe}_{0.5}$ as a function of pressure.

Since no experimental results are available to compare the results, comparison has been made with the alloy $\text{Fe}_{0.5}\text{Ti}_{0.5}$ [15,16]. The results of $\text{Fe}_{0.5}\text{Ti}_{0.5}$ alloy are given below:

For H, $D(\text{cm}^2/\text{s}) = 1.064 \times 10^{-3} \exp(-503.3 \text{ meV} / k_B T)$ [Ref-15].

For H, $D(\text{cm}^2/\text{s}) = 1.01 \times 10^{-3} \exp(-496 \text{ meV} / k_B T)$ [Ref-16].

For ^2H , $D(\text{cm}^2/\text{s}) = 0.82 \times 10^{-3} \exp(-512 \text{ meV} / k_B T)$ [Ref-16].

On comparison, it is observed that the activation energy in $\text{Ni}_{0.5}\text{Fe}_{0.5}$ is very much less than that in $\text{Fe}_{0.5}\text{Ti}_{0.5}$. According to figure 8, one can conclude that, unlike $\text{Cr}_{0.7}\text{Fe}_{0.3}$, the pressure does not influence much on the diffusion of hydrogen isotopes in the $\text{Ni}_{0.5}\text{Fe}_{0.5}$ system. Hence, the system $\text{Ni}_{0.5}\text{Fe}_{0.5}$ seems to be very good storage medium for hydrogen and deuterium.

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