

Diffusion of hydrogen and deuterium in $\text{Ni}_{0.5}\text{Fe}_{0.5}$ alloy – effect of pressure

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Abstract : The phonon dispersion in the substitutional fcc alloy $\text{Ni}_{0.5}\text{Fe}_{0.5}$ has been calculated theoretically by applying Born-von Karman formalism including interaction upto fifth neighbours. The Mean Square Displacement (MSD) of surrounding host atoms with hydrogen and deuterium interstitials using Green's function technique and scattering matrix formalism are investigated for the temperature range (500 K–1250 K) from normal pressure to 2.5 GPa pressure. The MSD of atoms surrounding the interstitial are found to be smaller than those of host crystal. The diffusion parameters for hydrogen and deuterium are calculated using reaction coordinate technique for the temperature and pressure ranges mentioned above. It is found that the activation energy for hydrogen diffusion is less than that of deuterium diffusion and the diffusivity ratio D_H/D_D approaches the value of 1.75 at higher temperatures. The results are compared with the existing results and a good agreement is observed.

Keywords : Phonon dispersion, mean square displacement, diffusion, activation energy.

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1. Introduction

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. 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. Hence, a theoretical study on this aspect is derived for the alloy $\text{Ni}_{0.5}\text{Fe}_{0.5}$. The $\text{Ni}_{0.5}\text{Fe}_{0.5}$ system forms substitutional face centered cubic structure with a small mass disorder at room temperature [1]. Each basis of the lattice is shared by the average atomic mass of this alloy. The effects of force constants and mass disorder are small for the alloy considered here. Hence, a Born-von Karman formalism using the average atomic mass and resulting in average force constants, can be used for this disordered alloy to compute the phonon dispersion [2]. When hydrogen is

pumped into this alloy under high pressure, hydrogen migrates through the host lattices by thermally activated jumps to neighbouring empty interstitial sites. The diffusion of hydrogen into this material is characterised by the diffusion coefficient $D = D_0 \exp(-E_a/k_B T)$ which determines its storing capacity.

The objective of this paper is to study the effect of pressure on the isotopic diffusion of hydrogen. The Mean Square Displacement value of the surrounding atoms with hydrogen and deuterium interstitials are evaluated using Green's function technique and scattering matrix formalism. The diffusion parameters are calculated using reaction coordinate technique in the α -phase of the $\text{Ni}_{0.5}\text{Fe}_{0.5}$ system under the influence of pressure at various temperatures (500 K to 1250 K).

2. Theory and method of calculation

The substitutional alloy $\text{Ni}_{0.5}\text{Fe}_{0.5}$ has the lattice constant $a_0 = 3.5868 \text{ \AA}$ at NTP [1]. In the adiabatic and harmonic

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approximation, the phonon frequencies of the normal modes of vibration of a cubic crystal are calculated by solving the secular equation

$$|D(q) - \omega^2(q)I| = 0, \quad (1)$$

where I is the unit matrix and D is the dynamical matrix which is given by

$$D_{k'k} = \frac{1}{m_k m_{k'}} \sum_{\alpha\beta} \Phi_{\alpha\beta} \exp(iq \cdot (R(l') - R(l))). \quad (2)$$

Here, q is the wave vector, m_k is the mass of the k -th atom in the l -th unit cell, $m_{k'}$ is the mass of the k' -th atom in the l' -th unit cell, $\Phi_{\alpha\beta} \begin{pmatrix} l & l' \\ k & k' \end{pmatrix}$ is the atomic force constant, $R(l)$ and $R(l')$ are the position vectors. The average atomic mass of the alloy $A_x B_{1-x}$ is determined from the relation

$$M_{A_x B_{1-x}} = xM_A + (1-x)M_B. \quad (3)$$

The dynamical matrix elements are evaluated according to Born-von Karman formalism extending to fifth neighbour interaction and is given in the Appendix. The matrix diagonalization is carried out for 73 wave vector points of the *fcc* lattice. The phonon frequency dispersion is calculated by solving eq. (1) using the computed force constant parameters given in Table 1.

The Green's function matrix of the metal atoms is calculated from the equation

$$g_{\alpha\beta} = \frac{1}{N \sqrt{m_k m_{k'}}} \sum_{q,j} \frac{e_\alpha(k|q,j) e_\beta^*(k'|q,j)}{(\omega_{\max}^2 - \omega_j^2(q))} \exp[2\pi i(q \cdot r(kk'))], \quad (4)$$

where N is the total number of cells in the unperturbed crystal, $e_\alpha(k|qj)$ is the α -th component of the eigen vectors of phonon (q, j) , r defines the distance of the k' -th atom in the l' -th cell from the k -th atom in the zeroth cell and ω_{\max} is the maximum angular frequency of the host crystal. When the alloy is loaded with hydrogen, it occupies the octahedral interstitial site [3]. With the interstitial atom in the $(0 \ 0 \ 0) a_0$ position, there are six nearest neighbour metal atoms at the positions

$$\left(\frac{1}{2} \ 0 \ 0\right) a_0, \left(\bar{\frac{1}{2}} \ 0 \ 0\right) a_0, \left(0 \ \frac{1}{2} \ 0\right) a_0,$$

Figure 1. Computed force constant parameters of $Ni_{0.5} Fe_{0.5}$ alloy at normal pressure.

Position of atoms (in a_0 units)	Force constant parameters	Force constant value (N/m)
$\begin{pmatrix} 1 & 1 \\ 2 & 2 \end{pmatrix} 0$	A_1	16.4800
	B_1	18.7200
	C_1	-1.2900
(100)	A_2	0.4500
	B_2	-0.0400
$\begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix}$	A_3	0.5700
	B_3	0.3000
	C_3	0.1500
	D_3	0.1900
(110)	A_4	0.4900
	B_4	0.4700
	C_4	-0.4100
$\begin{pmatrix} 3 & 1 \\ 2 & 2 \end{pmatrix} 0$	A_5	-0.3300
	B_5	-0.1400
	C_5	0.0400
	D_5	0.0800

$$\left(0 \ \bar{\frac{1}{2}} \ 0\right) a_0, \left(0 \ 0 \ \frac{1}{2}\right) a_0 \text{ and } \left(0 \ 0 \ \bar{\frac{1}{2}}\right) a_0$$

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

$$U_1 = \left\{ I + g(\delta l + a\gamma a^T) \left[I - g(\delta l + a\gamma a^T) \right]^{-1} \right\} U_{10}, \quad (5)$$

where the Green's function matrix g and the change in the dynamical matrix δl are of the order (18×18) , the metal-hydrogen interaction matrix a is of the order (18×3) .

The interstitial Green's function matrix γ is of the order (3×3) which is defined as

$$\gamma(\omega^2) = \left[m_s (\omega_j^2(q) - \omega_j^2) \right]^{-1} I, \quad (6)$$

where m_s is the mass of the interstitial atom, I is the unit matrix and ω_j is the vibrational frequency of the interstitial in the otherwise frozen lattice. The matrix U_{10} of order (18×1) 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

$$\xi = -\gamma a^T U_1. \quad (7)$$

Since U_{10} involves the inverse matrix which is complex in nature and is of the order (18 × 18), more computer time is needed. The defect space contains one interstitial atom and six equidistant atoms and only first neighbour interaction is considered. Therefore, even though the system is disordered, as a small group, the defect space is ordered one. Hence, the matrices g and δl are block-diagonalized using the symmetric coordinates for the O_h group [4] to reduce the computing time. The matrix a consists of force constant parameters representing metal-hydrogen interaction. The elements of a are fitted using the potential ϕ [5] which is of the form

$$\phi = -\left(\frac{\alpha}{r^4}\right) + \left(\frac{\beta}{r^8}\right).$$

Parameters α and β are fitted using the localized modes $\omega_H = 1.001335 \times 10^{14}$ rad s⁻¹ and $\omega_{2H} = 0.708051 \times 10^{14}$ rad s⁻¹ [3]. The mean square displacement values are calculated using the relation

$$\langle U_i^2(q, \omega) \rangle = \frac{1}{2} \int_0^\infty \frac{U^2(q, \omega)}{\omega} \coth\left(\frac{\hbar\omega}{2k_B T}\right) d\omega. \quad (8)$$

The diffusion coefficients of hydrogen in the alloy are calculated by applying reaction coordinate approach suggested by Flynn [6] in the limit of an elastic continuum. When hydrogen jumps from one interstitial position to the other, the neighbours exert a strong repulsive force on jumping atoms. The jump will be completed only if the fluctuations in the reaction coordinate of diffusing atom is sufficiently strong to force the moving atom past its neighbours towards the vacant position. To implement this, the reaction coordinate is derived as

$$\chi(q, j) = \left[\xi_d - \left(\frac{1}{m'}\right) \sum_{q,j} U_j \right] \cdot \hat{\chi} \quad (9)$$

with $j = 1, 2, 3, \dots, m'$,

where ξ_d is the displacement of diffusing atom and U_j refers the displacement of the j -th atom of m' neighbouring atoms obstructing the jump. Jump occurs only when the coordinate exceeds a critical value χ_c . The jump frequency of hydrogen has been obtained from Kac's equation [7] given as

$$\Gamma = \frac{\sum_{q,j} \omega^2(q, j) |\chi(q, j)|^2}{\sum |\chi(q, j)|^2} \exp\left(-\frac{\chi_c}{\chi}\right) \quad (10)$$

The critical value of the reaction coordinate χ_c is considered as 30% of the atomic radius of the metal atoms.

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

$$D = D_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (11)$$

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

$$D_0 = \Gamma_0 l^2 \quad (12)$$

where Γ_0 is the pre-exponential factor of the jump frequency and l is the 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 evaluated phonon frequency dispersion for normal pressure is shown in Figure 1 along with the inelastic slow neutron diffraction experimental data [2].

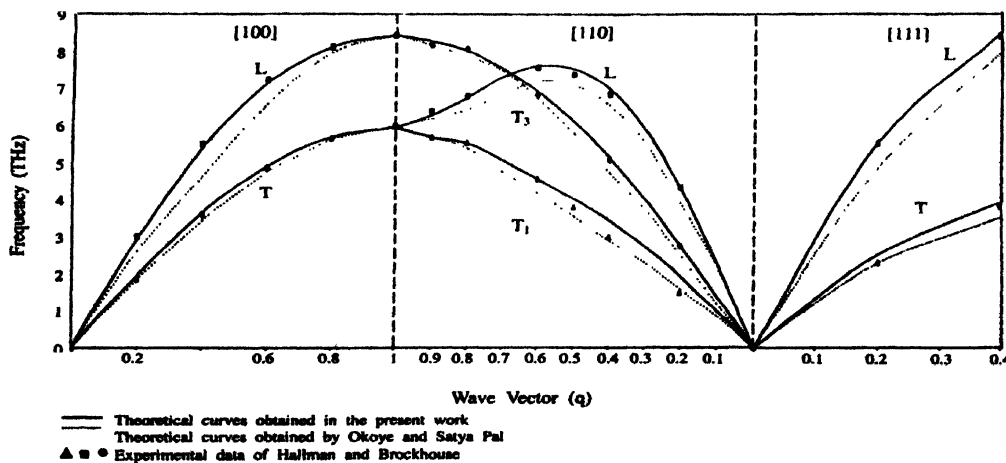


Figure 1. Phonon dispersion in Ni_{0.5}Fe_{0.5} alloy.

The theoretical result carried out in the frame work of transition metal-model potential approach [8] and the mean crystal model including a short range three body interaction model [9] worked out by Okoye and Satya Pal [10] is also shown in this figure. It is found that the computed values agree well with the experimental values whereas other theoretical values obtained [10] 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.

From the evaluated Green's function values, the MSD of the defect space atoms are calculated at 500 K, 750 K, 1000 K, 1250 K temperatures. It is found that the MSD of H/²H atoms are much larger than that of surrounding metal atoms. 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 in which as the vibrational amplitude of H dominates, naturally that of other one becomes smaller. The same trend has been observed experimentally for the NbH_x system [11–13]. The variation of MSD values with temperature for H and ²H interstitial under normal pressure are shown in Figures 2 and 3 respectively.

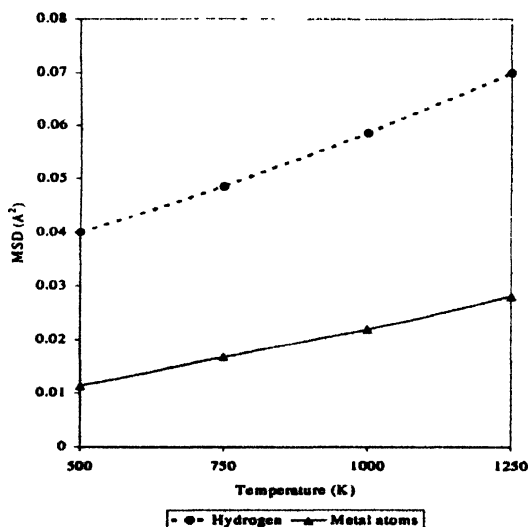


Figure 2. MSD of Ni_{0.5}Fe_{0.5} with hydrogen interstitial.

For both type of impurities, the MSD values increase with temperature and decrease with pressure as expected.

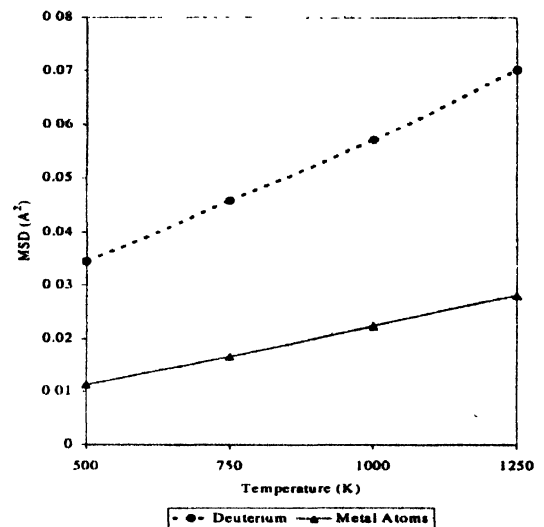


Figure 3. MSD of Ni_{0.5}Fe_{0.5} with deuterium interstitial.

The change in MSD with pressure is very small and the percentage of variation of MSD goes on decreasing in the higher pressure region. This is due to the shrinkage of the lattice.

The diffusion constants obtained for normal pressure is given below :

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

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

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 (773 K for Pd), *fcc* metals show the reverse isotope dependence on the activation energy. But the Ni_{0.5}Fe_{0.5} system shows the normal isotope effect *i.e.* $E_{a,H} < E_{a,2H}$ 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.

Since neither experimental nor other theoretical results are available to compare the results for this system except the study of isotopic diffusion in Ni [15], comparison has been made with the alloy Fe_{0.5}Ti_{0.5} [16,17].

The results of Fe_{0.5}Ti_{0.5} alloy are given below :

For H, D (cm²/s) = $1.064 \times 10^{-3} \exp(-503.3 \text{ meV} / k_B T)$ [Ref-16].

For H, D (cm²/s) = $1.01 \times 10^{-3} \exp(-496 \text{ meV}/k_B T)$ [Ref-17].

For ²H, D (cm²/s) = $0.82 \times 10^{-3} \exp(-512 \text{ meV}/k_B T)$ [Ref-17].

On comparison, it is observed that the activation energy in Ni_{0.5}Fe_{0.5} is very much less than that in Fe_{0.5}Ti_{0.5}. Also the variation of diffusion parameter with pressure in Ni_{0.5}Fe_{0.5} at the temperature of 500 K shown in Figure 4

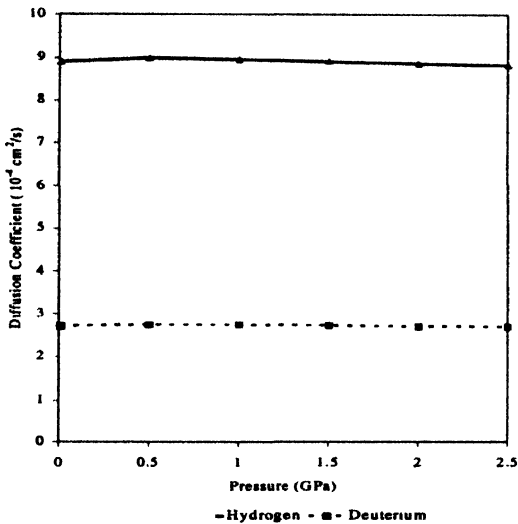


Figure 4. Diffusivity of H and ²H in Ni_{0.5}Fe_{0.5} alloy as a function of pressure at 500 K.

Appendix

Dynamical matrix elements of Ni_{0.5}Fe_{0.5} alloy :

$$D(1,1) = \frac{1}{Mass} [4A_1(\cos \pi q_x \cos \pi q_y + \cos \pi q_x \cos \pi q_z) + 4C_1 \cos \pi q_y \cos \pi q_z + 2A_2 \cos 2\pi q_x + 2B_2(\cos 2\pi q_y + \cos 2\pi q_z) + 8A_3 \cos 2\pi q_x \cos \pi q_y \cos \pi q_z + 8C_3 \cos \pi q_x (\cos 2\pi q_y \cos \pi q_z + \cos \pi q_y \cos 2\pi q_z) + 4A_4(\cos 2\pi q_x \cos 2\pi q_y + \cos 2\pi q_x \cos 2\pi q_z) + 2C_4 \cos 2\pi q_y \cos 2\pi q_z + 4A_5(\cos 3\pi q_x \cos \pi q_y + \cos 3\pi q_x \cos \pi q_z) + 4C_5(\cos \pi q_x \cos 3\pi q_y + \cos \pi q_x \cos 3\pi q_z) + 4D_5(\cos \pi q_y \cos 3\pi q_z + \cos 3\pi q_y \cos \pi q_z)].$$

indicates that the pressure does not influence much on the diffusion of hydrogen isotopes in the system of study at hand. Hence, the system of study seems to be very good storage medium for hydrogen and deuterium.

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$$D(1,2) = \frac{-1}{Mass} [4B_1 \sin \pi q_x \sin \pi q_y + 8B_3(\sin 2\pi q_x \sin \pi q_y \cos \pi q_z + \sin 2\pi q_y \sin \pi q_x \cos \pi q_z) + 8D_3 \cos 2\pi q_z \sin \pi q_x \sin \pi q_y + 4B_4 \sin 2\pi q_x \sin 2\pi q_y + 4B_5(\sin 3\pi q_x \sin \pi q_y + \sin \pi q_x \sin 3\pi q_y)].$$

$$D(1,3) = \frac{-1}{Mass} [4B_1 \sin \pi q_x \sin \pi q_z + 8B_3(\sin 2\pi q_x \sin \pi q_z \cos \pi q_y + \sin 2\pi q_z \sin \pi q_x \cos \pi q_y) + 8D_3 \cos 2\pi q_y \sin \pi q_x \sin \pi q_z + 4B_4 \sin 2\pi q_y \sin 2\pi q_z + 4B_5(\sin 3\pi q_x \sin \pi q_z + \sin \pi q_x \sin 3\pi q_z)].$$

$$D(2,1) = D(1,2)$$

$$D(2,2) = \frac{1}{Mass} [4A_1(\cos \pi q_x \cos \pi q_y + \cos \pi q_y \cos \pi q_z) + 4C_1 \cos \pi q_x \cos \pi q_z + 2A_2 \cos 2\pi q_y + 2B_2(\cos 2\pi q_x + \cos 2\pi q_z) + 8A_3 \cos 2\pi q_y \cos \pi q_x \cos \pi q_z + 8C_3 \cos \pi q_y (\cos 2\pi q_x \cos \pi q_z + \cos \pi q_x \cos 2\pi q_z) + 4A_4(\cos 2\pi q_x \cos 2\pi q_y + \cos 2\pi q_y \cos 2\pi q_z) + 2C_4 \cos 2\pi q_x \cos 2\pi q_z + 4A_5(\cos 3\pi q_y \cos \pi q_x + \cos 3\pi q_y \cos \pi q_z) + 4C_5(\cos \pi q_y \cos 3\pi q_x + \cos \pi q_y \cos 3\pi q_z) + 4D_5(\cos \pi q_x \cos 3\pi q_z + \cos 3\pi q_x \cos \pi q_z)].$$

$$D(2,3) = \frac{-1}{Mass} [4B_1 \sin \pi q_y \sin \pi q_z + 8B_3(\sin 2\pi q_y \sin \pi q_z \cos \pi q_x + \sin 2\pi q_z \sin \pi q_y \cos \pi q_x) + 8D_3 \cos 2\pi q_x \sin \pi q_y \sin \pi q_z + 4B_4 \sin 2\pi q_y \sin 2\pi q_z + 4B_5(\sin 3\pi q_y \sin \pi q_z + \sin \pi q_y \sin 3\pi q_z)].$$

$$D(3,1) = D(1,3).$$

$$D(3,2) = D(2,3).$$

$$D(3,3) = \frac{1}{Mass} [4A_1(\cos \pi q_x \cos \pi q_z + \cos \pi q_y \cos \pi q_z) + 4C_1 \cos \pi q_x \cos \pi q_y + 2A_2 \cos 2\pi q_z + 2B_2(\cos 2\pi q_x + \cos 2\pi q_y) + 8A_3 \cos 2\pi q_z \cos \pi q_x \cos \pi q_y + 8C_3 \cos \pi q_z (\cos 2\pi q_x \cos \pi q_y + \cos \pi q_x \cos 2\pi q_y) + 4A_4(\cos 2\pi q_x \cos 2\pi q_z + \cos 2\pi q_y \cos 2\pi q_z) + 2C_4 \cos 2\pi q_x \cos 2\pi q_y + 4A_5 \cos 3\pi q_z (\cos \pi q_x + \cos \pi q_y) + 4C_5(\cos \pi q_z \cos 3\pi q_x + \cos \pi q_z \cos 3\pi q_y) + 4D_5(\cos \pi q_x \cos 3\pi q_y + \cos 3\pi q_x \cos \pi q_y)].$$

Here, q_x, q_y, q_z are the x, y, z components of the wave vector and $Mass$ is the average atomic mass of the system.