

# Lattice Dynamics of Hydrogen Interstice in $\text{Co}_{0.92}\text{Fe}_{0.08}$

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**Abstract:** Lattice dynamics of hydrogen interstice in the binary alloy  $\text{Co}_{0.92}\text{Fe}_{0.08}$  has been carried out to calculate the phonon dispersions along the [100], [110], [111] directions. The phonon density of states, variation of specific heat capacity and Debye's temperature with temperature are also calculated. A reasonably good agreement is found between the calculated and other theoretical and experimental results. The mean square displacement (MSD) of atoms surrounding the interstitial hydrogen atom is reported along with the defect modes.

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## 1. Introduction

Hydrogen interstice and hence hydrogen storage in metals and alloys is a current subject of considerable experimental and theoretical investigations. A relatively small number of theoretical works have focused on diffusion in pure metals at high interstitial concentration [1-2]. The diffusion of interstitial hydrogen in metals is known to depend strongly on the host metal. Host metal properties such as lattice type, electronic structure and elastic moduli are thought to play key roles in determining the diffusion rate of hydrogen [3]. At higher hydrogen contents more complicated permeation behaviour is observed. First of all, understanding the transport of hydrogen through thin metallic films is essential for the development of coatings preventing bulk materials from hydrogen

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uptake [4]. Although some approaches in the form of Green's function technique and molecular dynamics [5-8] have been used to explain the lattice dynamics of alloys, most of the theoretical work has been done in terms of the coherent potential approximations and their modifications [9-11].

Recent research in this field shows that binary alloys are effective storage media of hydrogen [12-13]. Hydrogen in binary alloys such as  $\text{Fe}_{0.5}\text{Ti}_{0.5}$ [14-15],  $\text{Ni}_{0.5}\text{Fe}_{0.5}$  and  $\text{Cr}_{0.7}\text{Fe}_{0.3}$ [16] have been intensively investigated by both the experimental and theoretical methods. Various theoretical models such as Born - von Karman model [17], three body electron gas phenomenological force model [18] and the transition metal model potential (TMMP) of Animalu [19] were derived to compute the phonon dispersions curves for  $\text{Co}_{0.92}\text{Fe}_{0.08}$  alloy is also found to be the best media to store hydrogen. This alloy forms a substitutional face centered cubic (fcc) structure, with lattice constant 0.355nm [20]. The phonon frequencies for this alloy for the symmetry directions have been measured using the inelastic neutron scattering technique [21]. Phonon dispersion of  $\text{Co}_{0.92}\text{Fe}_{0.08}$  has been calculated theoretically using the TMMP by Animalu [19]. Shyam et al [20] employed the TMMP model to study the dynamical behaviour of  $\text{Co}_{0.92}\text{Fe}_{0.08}$  in which force constants are calculated up to tenth nearest neighbours and hence computed the phonon dispersion. The authors [20] also have reported the phonon frequency distribution, specific heat capacity, variation of Debye's temperature with temperature and the mean square displacement of surrounding atoms to the hydrogen interstice.

To understand the nature of hydrogen diffusion, knowledge of defect modes and displacement of the surrounding atoms to the defect is required. With this motivation in mind, this theoretical investigation has been carried out. Since the neutron diffraction experimental results are analysed on the basis of Born-von Karman model considering interactions up to sixth neighbours, it is easy to get the force constant parameters from the literature. Hence the same model has been used to work out the phonon dispersion and the phonon frequency distribution. The Green's function technique and the scattering matrix formalism have been used to calculate the MSD values of atoms surrounding the hydrogen defect and the defect modes. Our results are comparable with the existing experimental and other theoretical results.

## 2. Method Of Calculation

The Born-von Karman formalism has been employed to formulate the dynamical matrix for  $\text{Co}_{0.92}\text{Fe}_{0.08}$  system by considering the interactions up to sixth nearest neighbours. The values of the calculated force constant parameters are given in Table 1. These parameters are procured from the literature [21], which are fitted using neutron diffraction data. The elements of the dynamical matrix are given in Appendix 1.

Diagonalisation of the dynamical matrix yields the phonon frequencies and eigen vectors. The diagonalisation is carried out using a set of 3871 wave vector points obtained by uniformly dividing the Brillouin zone. With the calculated frequency distribution,

specific heat capacity has been calculated using Debye's equation,

$$C_v = 9Nk_B \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2} \quad (1)$$

where  $x = \frac{\hbar\omega}{k_B T}$ ,  $k_B$  is the Boltzmann constant,  $N$  is the number of atoms,  $\omega$  is the frequency of normal mode of vibrations and  $\theta_D$  is the Debye's temperature.

Hydrogen interstice in  $\text{Co}_{0.92}\text{Fe}_{0.08}$  alloy occupies the minimum energy position namely the octahedral position with  $O_h$  symmetry as shown in Fig. 1. The presence of the defect can alter the frequency of normal modes of vibration and the atomic displacements due to the change in atomic force constant. Because of the defects, any one or all types of defect modes such as localised vibrational modes, gap modes and resonant modes may arise. The changes in the normal modes of vibration by the presence of defects lead to considerable changes in the thermodynamic and kinetic properties of the system. Hence it is essential to study the defect modes in detail.

The Green's function technique is an effective mathematical tool for investigating the defect modes and the amplitude of vibration of the atoms affected by defects. Following Maradudin et al. [22]. Green's function matrix can be written in terms of eigen values and eigen vectors as

$$G_{\alpha\beta} \left( \begin{matrix} l & l' \\ k & k' \end{matrix}; \omega^2 \right) = \frac{1}{N\sqrt{m_k m_{k'}}} \sum \frac{\vec{e}_\alpha(k/\vec{q}j) \vec{e}_\beta(k'/\vec{q}j)}{(\omega_{max}^2 - \omega_j^2(\vec{q}))} [\exp(i\vec{q} \cdot (\vec{R}(l) - \vec{R}(l')))] \quad (2)$$

where  $\omega_{max}$  is the maximum frequency among all normal modes of the host crystal. Green's function technique and scattering matrix formalism [22] have been used to evaluate the defect modes and the displacement of neighbours to the interstitial atom. The defect modes are obtained by solving the equation,

$$\Delta(\omega^2) = |I - g(\delta l + a\gamma a^T)| = 0 \quad (3)$$

where  $I$  is a unit matrix of order (18 x 18),  $g$  is a Green's function matrix of order (18 x 18),  $\delta l$  is the change in dynamical matrix due to the introduction of defect which is also of the order (18 x 18), 'a' is (18 x 3) matrix representing interaction of hydrogen with neighbours,  $\gamma$  is the interstitial Green's function matrix of order (3x3). The force constant parameters representing hydrogen – metal interactions in the 'a' matrix elements are calculated using the potential form discussed by Machlin [23]. The displacement of neighbouring atoms surrounding the interstitial is obtained using the equation,

$$u_1 = \{I + g(\delta l + a\gamma a^T)[I - g(\delta l + a\gamma a^T)]^{-1}\} u_\alpha \quad (4)$$

$u_\alpha$  is given by

$$u_\alpha \left( \begin{matrix} l \\ k \end{matrix}; \vec{q}j \right) = \left\{ \frac{h}{2Nm_k \omega_{qj}} \right\}^{1/2} e_\alpha(k, \vec{q}j) \exp \left[ i\vec{q} \cdot r \left( \begin{matrix} l \\ k \end{matrix} \right) \right] \quad (5)$$

where  $\omega_{q_j}$  is the frequency of normal mode of vibration and  $e_\alpha(k, \vec{q}_j)$  is the eigen vector. The mean square displacement at a particular temperature T is obtained by the equation,

$$\langle u_1^2 \rangle = \frac{1}{2} \int_0^\infty \frac{u_1^2(k, \omega_{q_j})}{\omega_{q_j}} \coth\left(\frac{\hbar\omega_{q_j}}{2k_B T}\right) d\omega_{q_j} \quad (6)$$

### 3. Results And Discussion

The values of the force constants of  $\text{Co}_{0.92}\text{Fe}_{0.08}$  alloy are fed into the dynamical matrix and then secular equation is first solved to obtain the dispersion relations along the three high symmetry directions [100], [110] and [111]. The phonon dispersion curves, so computed are plotted along with the result of Shyam et al. [20] and are shown in Fig.2. The solid line denotes the calculated result and square, triangle and circle markers denote the experimental result [21]. It has been found that the present results agree reasonably well with the experimental data.

The calculated phonon density of states is shown in Fig. 3 along with the result of Shyam et al. [20]. The agreement is found to be good. Using the calculated phonon density of states, the specific heat variation with temperature for the range 0K to 250K has been calculated and is shown in Fig. 4 along with the computed result of Shyam et al. [20]. It has been found that the present result is in good agreement with the result of Shyam et al. [20]. The phonon density based Debye's temperature variation with temperature has been calculated for the temperature range 0K to 300K and is shown in Fig. 5 along with the result of Shyam et al. [20] and both the results are found to be in good agreement.

When the hydrogen interstitial atom occupies the octahedral positions of the fcc lattice, the metal atoms close to it, relax from their equilibrium positions due to the coupling between the interstice and metal atoms. The Green's function values for this defect space have been evaluated and using these values, the MSD of the defect space atoms are calculated for temperatures 250K, 500K, 750K, and 1000K. The variation of the MSD with and without hydrogen interstice in  $\text{Co}_{0.92}\text{Fe}_{0.08}$  with temperatures is shown in Fig. 6. It is clear from that figure that MSD values increase with temperature as expected. The MSD values of host atoms are greatly reduced by the inclusion of hydrogen atom. The reduction is caused by the change in coupling constants between the atoms and the defect space due to the local expansion of the lattice by the presence of interstice. This reduction is also due to the lightest mass of hydrogen atom which when makes resonant mode of vibration, the surrounding atoms tend to be at rest. Hence our model is realistic fetches reasonable results.

Using the Green's function technique and scattering matrix formalism the localised vibrational modes have been worked out for the hydrogen atom as an interstitial defect in the  $\text{Co}_{0.92}\text{Fe}_{0.08}$  system. The localized mode falls at  $531 \text{ cm}^{-1}$ . Due to the lighter hydrogen the vibrational amplitude is very large in comparison with host case. Due to the cubic symmetry the localized mode is triply degenerate. Hence only one mode is

reported.

## Conclusion

The present lattice dynamical investigation obviously indicates the reduction of MSD value of the  $\text{Co}_{0.92}\text{Fe}_{0.08}$  alloy with hydrogen as interstitial defect. Since MSD is directly related with Debye Waller factor through the equation  $W(\mathbf{k}) = (8\pi^2/3)\langle u^2 \rangle$ , it can be used to find out the intensity of scattering in the X-ray diffraction studies. This result can be verified by the experimentalists for this alloy of study with hydrogen as interstice.

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**Table – 1. Force constant parameters in units of  $10^4$  dynes  $\text{cm}^{-1}$** 

Parameters	Values
A <sub>1</sub>	1.69
B <sub>1</sub>	1.78
C <sub>1</sub>	-0.09
A <sub>2</sub>	-0.30
B <sub>2</sub>	-0.05
A <sub>3</sub>	0.04
B <sub>3</sub>	0.007
C <sub>3</sub>	0.02
D <sub>3</sub>	0.014
A <sub>4</sub>	0.09
B <sub>4</sub>	0.12
C <sub>4</sub>	-0.03
A <sub>5</sub>	0.009
B <sub>5</sub>	0.022
C <sub>5</sub>	-0.012
D <sub>5</sub>	0.023
A <sub>6</sub>	0.052
B <sub>6</sub>	0.035

## Appendix I

The elements of the dynamical matrix are given below:

$$D(1,1) = \frac{1}{m} [4A_1 ((\cos\pi q_x \cos\pi q_z + \cos\pi q_x \cos\pi q_y) - 2) + 4C_1 (\cos\pi q_y \cos\pi q_z - 1) + 2A_2 (\cos 2\pi q_x - 1) + 2B_2 (\cos 2\pi q_y - 1) + 2B_2 \cos 2\pi q_z - 1) + 8C_3 ((\cos\pi q_x \cos\pi q_y \cos 2\pi q_y + \cos\pi q_x \cos\pi q_y \cos\pi q_z) - 2) + 8A_3 (\cos 2\pi q_x \cos\pi q_y \cos\pi q_z - 1) + 4A_4 ((\cos 2\pi q_x \cos 2\pi q_y + \cos 2\pi q_x \cos 2\pi q_z) - 2) + 4C_4 (\cos 2\pi q_y \cos\pi q_z - 1) + 4A_5 (\cos 3\pi q_x \cos\pi q_z + \cos 3\pi q_x \cos\pi q_y) - 2) + 4D_5 ((\cos\pi q_x \cos 3\pi q_y + \cos\pi q_x \cos 3\pi q_y) - 2) + 4C_5 ((\cos\pi q_x \cos 3\pi q_y + \cos\pi q_x \cos 3\pi q_z) - 2) + 8A_6 (\cos 2\pi q_x \cos 2\pi q_y \cos 2\pi q_z - 1)]$$

$$D(2, 2) = \frac{1}{m} [4C_1 (\cos\pi q_x \cos\pi q_z - 1) + 4A_1 ((\cos\pi q_x \cos\pi q_y + \cos\pi q_y \cos\pi q_z) - 2) + 2B_2 ((\cos 2\pi q_x + \cos 2\pi q_z) - 2) + 2A_2 (\cos 2\pi q_y - 1) + 8C_3 ((\cos 2\pi q_x \cos\pi q_y \cos\pi q_z + \cos\pi q_x \cos\pi q_y \cos 2\pi q_z) - 2) + 8A_3 (\cos\pi q_x \cos 2\pi q_y \cos\pi q_z - 1) + 4A_4 (\cos 2\pi q_x \cos 2\pi q_y - 1) + 2A_4 (\cos 2\pi q_z \cos 2\pi q_y - 1) + 4C_4 (\cos 2\pi q_x \cos 2\pi q_z - 1) + 4D_5 ((\cos 3\pi q_x \cos\pi q_z + \cos\pi q_x \cos 3\pi q_z) - 2) + 4C_5 ((\cos 3\pi q_x \cos\pi q_y + \cos\pi q_y \cos 3\pi q_z) - 2) + 4A_5 ((\cos 3\pi q_y \cos\pi q_z + \cos\pi q_x \cos 3\pi q_y) - 2) + 8A_6 (\cos 2\pi q_x \cos 2\pi q_y \cos 2\pi q_z - 1)].$$

$$D(3, 3) = \frac{1}{m} [4A_1 ((\cos\pi q_x \cos\pi q_z + \cos\pi q_y \cos\pi q_z) - 2) + 4C_1 (\cos\pi q_x \cos\pi q_y - 1) + 2B_2 ((\cos 2\pi q_x + \cos 2\pi q_y) - 2) + 2A_2 (\cos 2\pi q_z - 1) + 8A_3 (\cos\pi q_x \cos\pi q_y \cos 2\pi q_z - 1) + 8C_3 ((\cos 2\pi q_x \cos\pi q_y \cos\pi q_z + \cos\pi q_x \cos 2\pi q_y \cos\pi q_z) - 2) + 4C_4 (\cos 2\pi q_y \cos 2\pi q_x - 1) + 4A_4 ((\cos 2\pi q_y \cos 2\pi q_z + \cos 2\pi q_x \cos 2\pi q_z) - 2) + 4C_5 ((\cos 3\pi q_x \cos\pi q_z + \cos 3\pi q_y \cos\pi q_z) - 2) + 4D_5 ((\cos\pi q_x \cos 3\pi q_y + \cos 3\pi q_x \cos\pi q_z) - 2) + 4A_5 ((\cos\pi q_y \cos 3\pi q_z + \cos\pi q_x \cos 3\pi q_z) - 2) + 8A_6 (\cos 2\pi q_x \cos 2\pi q_y \cos 2\pi q_z - 1)]$$

$$D(1, 2) = \frac{1}{m} [-4B_1 (\sin\pi q_x \sin\pi q_y) - 8B_3 (\sin 2\pi q_x \sin\pi q_y \cos\pi q_z + \sin\pi q_x \sin 2\pi q_y \cos\pi q_z) - 8D_3 (\sin\pi q_x \sin\pi q_y \cos 2\pi q_y) - 4B_4 (\sin 2\pi q_x \sin 2\pi q_y) - 4B_5 (\sin 3\pi q_x \cos\pi q_y + \sin\pi q_x \sin 3\pi q_y) - 8B_6 (\sin 2\pi q_x \sin 2\pi q_y \cos 2\pi q_z)]$$

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

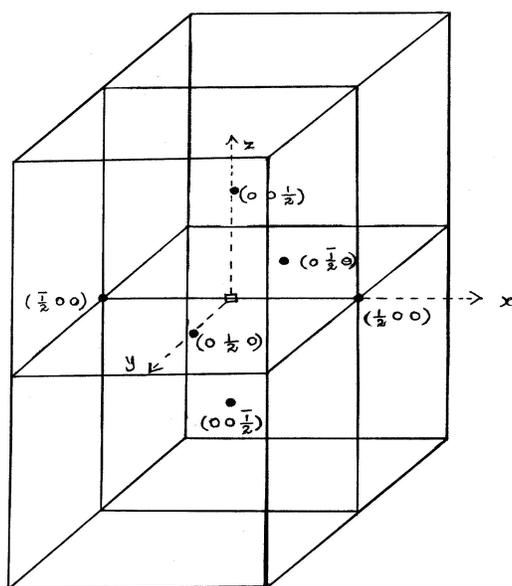
$$D(1, 3) = \frac{1}{m} [-4B_1 (\sin\pi q_x \sin\pi q_z) - 8B_3 (\sin 2\pi q_x \sin\pi q_z - \sin\pi q_x \cos\pi q_y \sin 2\pi q_z) - 8D_3 (\sin\pi q_x \cos 2\pi q_y \sin\pi q_y) - 4B_4 (\sin 2\pi q_x \sin 2\pi q_z) - 4B_5 (\sin\pi q_x \sin 3\pi q_z + \sin 3\pi q_y \sin\pi q_z) - 8B_6 (\sin 2\pi q_x \cos 2\pi q_y \sin 2\pi q_z)]$$

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

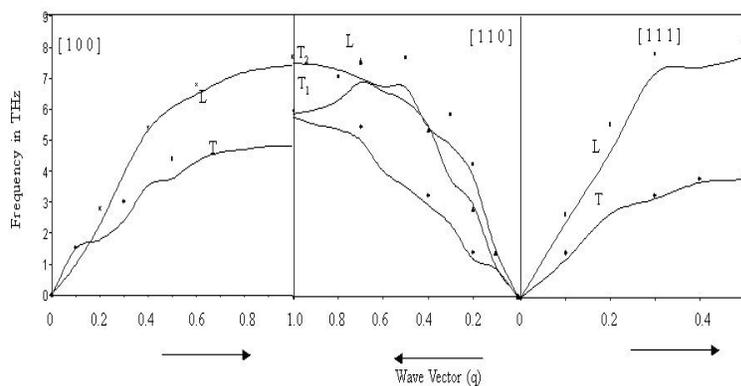
$$D(2, 3) = \frac{1}{m} [-4B_1 (\sin\pi q_y \sin\pi q_z) - 8D_3 (\cos 2\pi q_x \sin 2\pi q_y \sin\pi q_z) - 8B_3 (\cos\pi q_x \sin 2\pi q_y \sin\pi q_z + \cos\pi q_x \sin\pi q_y \sin 2\pi q_z) - 4B_4 (\sin 2\pi q_y \sin 2\pi q_z) - 4B_5 (\sin 3\pi q_y \sin\pi q_z + \sin\pi q_y \sin 3\pi q_z) - 8B_6 (\cos 2\pi q_x \sin 2\pi q_y \sin 2\pi q_z)].$$

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

Where  $A_1, B_1$  and  $C_1$ ;  $A_2, B_2$ ;  $A_3, B_3, C_3, D_3$ ;  $A_4, B_4, C_4$ ;  $A_5, B_5, C_5, D_5$  and  $A_6, B_6$  respectively are the force constants for the first to sixth neighbour interactions,  $m$  is statistical average mass and  $q_x, q_y, q_z$  are x, y and z components of wave vector.



**Fig. 1** Defect Space of H in  $Co_{0.92}Fe_{0.08}$  (□ H atom, ● Metal atom)



●, ▲ Result of Shapiro, et al. [21] , — Calculated result

**Fig. 2** Phonon Dispersion Curve for  $Co_{0.2}Fe_{0.08}$  Alloy

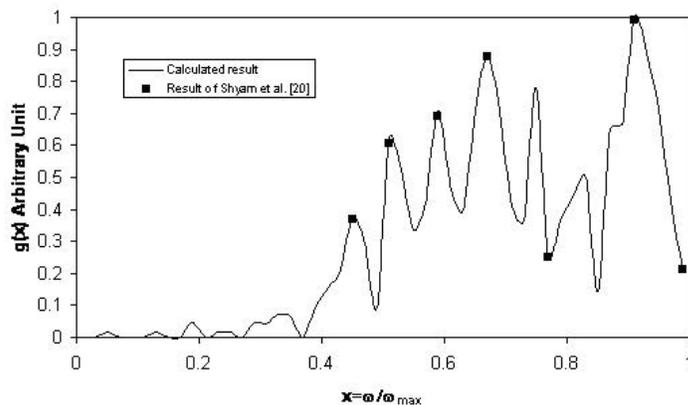


Fig. 3 Frequency distribution for  $Co_{0.92}Fe_{0.08}$

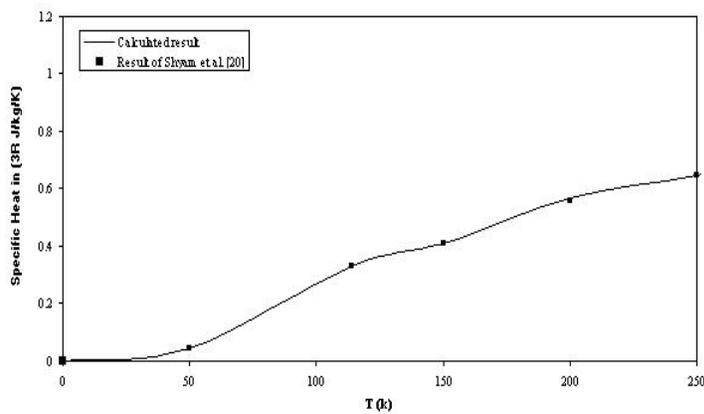


Fig. 4 Variation of the specific Heat of the  $Co_{0.92}Fe_{0.08}$  Alloy with Temperature

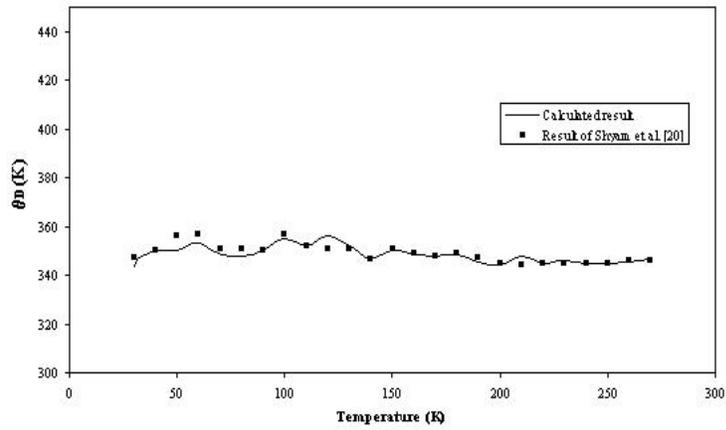


Fig. 5 Temperature dependence of the Debye's Temperature for the  $Co_{0.92}Fe_{0.08}$  Alloy

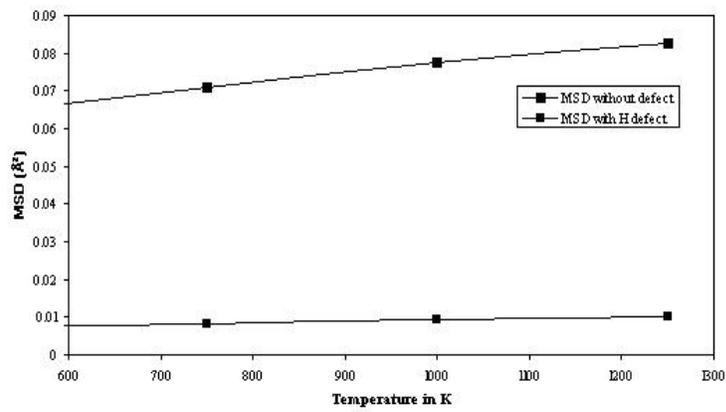


Fig. 6 MSD values for  $Co_{0.92}Fe_{0.08}$