



Pressure dependent hydrogen isotopic diffusion in $\text{Cr}_{0.7}\text{Fe}_{0.3}$ alloy

M Stalin Mano Gibson* and N Lawrence¹

Department of Physics, Mepeo Schlenk Engineering College, Sivakasi, Virudhunagar-626 005, Tamil Nadu, India

¹Department of Physics, St. Joseph's College, Tiruchirappalli-620 002, Tamil Nadu, India

E mail : manogibson@yahoo.com

Received 5 September 2005, accepted 17 January 2006

Abstract : Using Born-von Karman formalism including upto sixth nearest neighbours interaction, the phonon dispersion has been calculated theoretically in the substitutional *bcc* alloy $\text{Cr}_{0.7}\text{Fe}_{0.3}$. It is found to be in good agreement with the experimental results. The Mean Square Displacement (MSD) of surrounding host atoms with hydrogen and deuterium interstitials are investigated using Green's function technique and scattering matrix formalism from normal pressure to 2.5 GPa in the temperature range of 500 K–1250 K. The MSD of atoms surrounding the interstitial are found to be smaller than those of the host crystal atoms. Using reaction coordinate technique, the diffusion parameters are calculated for the above mentioned temperature and pressure ranges. It is observed that the activation energy for the diffusion of ^2H is twice as that for H diffusion and the diffusivity ratio $D_H / D_{^2H}$ is always greater than unity and it is temperature and pressure dependent.

Keywords : Phonon dispersion, diffusion, mean square displacement, activation energy, isotopic diffusion, Born-von Karman formalism.

PACS Nos. : 63.20.Dj, 66.30.Jt

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. 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* 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 Holstein [1] in which the tunneling matrix element J between neighbouring interstitial sites is treated as a perturbation to the total Hamiltonian, and accordingly, only non-adiabatic processes are allowed in calculating the jump frequency. In fact, Emin *et al* [2] demonstrated that the actual migration process of

hydrogen isotopes in *bcc* metals can be rather close to the adiabatic limit.

In the present work, the diffusion of hydrogen and deuterium in the *bcc* substitutional alloy $\text{Cr}_{0.7}\text{Fe}_{0.3}$ has been reported in which Born-von Karman formalism with average atomic mass is used to compute the phonon dispersion keeping adiabatic and harmonic approximations. 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 500 K – 1250 K with normal to 2.5G Pa pressure by applying Green's function technique and scattering matrix

*Corresponding Author

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 $\text{Cr}_{0.7}\text{Fe}_{0.3}$ has a *bcc* structure with lattice constant $a_0 = 2.877 \text{ \AA}$. The phonon frequencies of the normal modes of vibration are calculated by solving the secular equation

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

where D , the dynamical matrix is given by

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

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 and the elements are given in the Appendix. The force constant parameters used for the calculation of phonon dispersion are arranged in Table 1. The matrix diagonalization is carried out for 73 wave vector points of the *bcc* lattice. With hydrogen in one of the octahedral

Table 1. Force constant parameters of $\text{Cr}_{0.7}\text{Fe}_{0.3}$ alloy for normal pressure.

Force constant parameter	Force constant value (N/m)
1XX	12.013
1XY	12.553
2XX	20.980
2XY	-0.170
3XX	0.940
3XY	0.470
3ZZ	0.470
4XX	-0.135
4XY	-0.1291
4XZ	-0.389
4ZZ	-1.171
5XX	2.973
5XY	2.083
6XX	3.430
6XY	-1.840

position $(0\ 0\ 0) a_0$, there are two nearest neighbour metal atoms at $(0\ 0\ \frac{1}{2}) a_0$ and $(0\ 0\ -\frac{1}{2}) a_0$ positions and four next nearest neighbour metals at the positions, $(\frac{1}{2}\ \frac{1}{2}\ 0) a_0$, $(\frac{1}{2}\ \frac{1}{2}\ 0) a_0$, $(\frac{1}{2}\ \frac{1}{2}\ 0) a_0$ and $(\frac{1}{2}\ \frac{1}{2}\ 0) a_0$. The displacement of the six metal atoms in the defect space are calculated using the relation

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

and the (18×18) Green's function matrix g of the metal atoms is calculated from the equation

$$g_{\alpha\beta} \begin{pmatrix} 0 & l \\ k & k' \end{pmatrix} = \frac{1}{N\sqrt{m_k m_{k'}}} \sum_{q,j} \frac{e_{\alpha}(k|qj) e_{\beta}^*(k'|qj)}{(\omega_{\max}^2 - \omega_j^2(q))} \times \exp[2\pi i(q \cdot r(kk'))], \quad (3)$$

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 the 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 (reference cell) and ω_{\max} is the maximum angular frequency of the host crystal. The change in the dynamical matrix δl of order (18×18) is calculated from Morse potential and the elements of metal-hydrogen interaction matrix a of order (18×3) are fitted with a potential form $\phi = -\alpha/r_4 + \beta/r_8$ discussed by Machlin [4]. Parameters α and β are fitted with the following localized modes.

For hydrogen, $\omega_1 = 1.67040 \times 10^{14} \text{ rad s}^{-1}$ and $\omega_2 = 2.73352 \times 10^{14} \text{ rad s}^{-1}$.

For deuterium, $\omega_1 = 1.19377 \times 10^{14} \text{ rad s}^{-1}$ and $\omega_2 = 1.69641 \times 10^{14} \text{ rad s}^{-1}$.

The (3×3) interstitial Green's function matrix γ is defined as

$$\gamma(\omega^2) = \left[m_i (\omega_j^2(q) - \omega_i^2) \right]^{-1} I, \quad (5)$$

where m_i is the mass of the interstitial atom and ω_i is the vibrational frequency of the interstitial in the otherwise frozen lattice. The γ matrix is found to be of the form

$$\begin{pmatrix} \gamma_1 & 0 & 0 \\ 0 & \gamma_1 & 0 \\ 0 & 0 & \gamma_2 \end{pmatrix}. \quad \text{The matrix } U_{10} \text{ of order } (18 \times$$

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

$$\xi = -\gamma a^T U_1 \quad (6)$$

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

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

and the diffusion coefficients of hydrogen in the alloy are calculated by applying reaction coordinate approach suggested by Flynn [5] 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

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

with $j = 1, 2, 3, \dots, m'$. (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 Kac's equation [6] which is given as

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

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

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

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

$$D_0 = \Gamma_0 l^2 / 6 \quad (11)$$

with Γ_0 and l are respectively, the pre-exponential factor of the jump frequency and the jump distance.

3. Results and discussion

The calculated phonon frequencies of the $Cr_{0.7}Fe_{0.3}$ system using Born-von Karman model are shown in Figure 1 along with the existing experimental results measured using

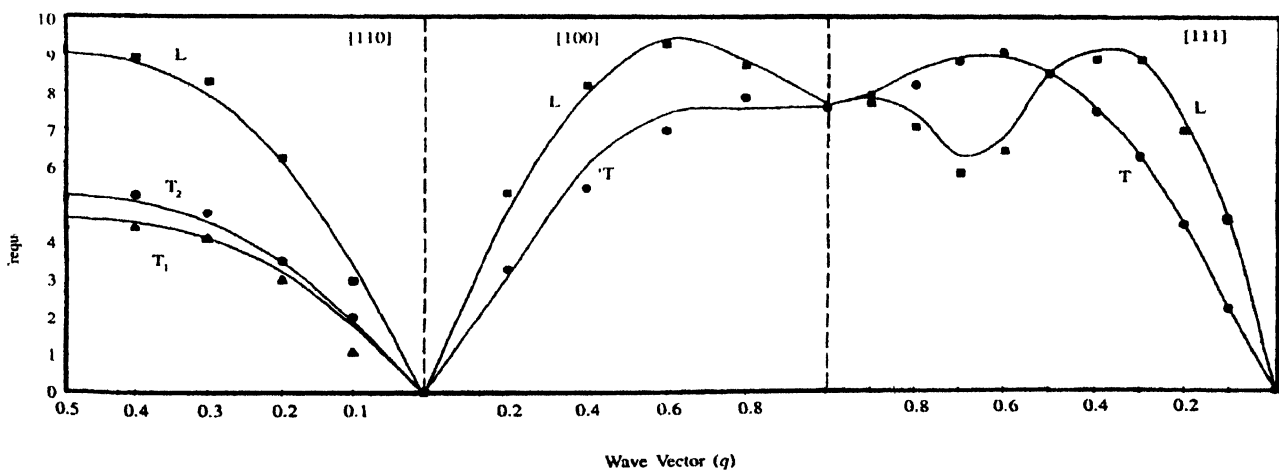


Figure 1. Phonon dispersion in $Cr_{0.7}Fe_{0.3}$ alloy. Solid curves represent the calculations by taking 6 nearest neighbours in the present work. $\blacksquare, \blacktriangle$ Experimental points of Lloyd *et al.*

the neutron inelastic scattering [7] 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 dispersion curves described by the *bcc* model was calculated and is plotted in Figure 2. It can be seen that the various peaks in this phonon distribution

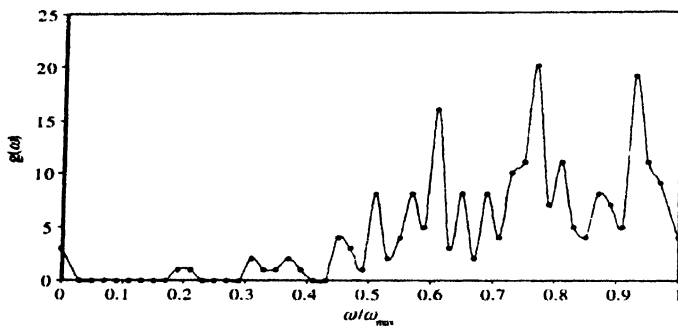


Figure 2. Phonon frequency distribution curve for $\text{Cr}_{0.7}\text{Fe}_{0.3}$ alloy at normal pressure.

curve correspond to the high phonon density regions of the dispersion curves. The phonon frequencies are worked out for higher pressures by evaluating the force constants and it is observed that the frequencies increase with increase in the pressure as expected. But no remarkable deviation is observed in the frequency distribution for higher pressures. Hence, the frequency distribution curve at normal pressure alone is shown.

The H / ^2H interstitial atom occupies the octahedral positions of the *bcc* lattice and 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 are evaluated using the eigen vectors from the phonon dispersion calculation. With the help of the Green's function values, the MSD of defect space atoms are found for the temperatures 500 K, 750 K, 1000 K and 1250 K. 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

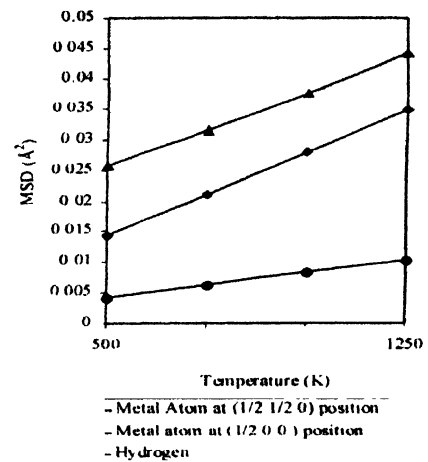


Figure 3. MSD of $\text{Cr}_{0.7}\text{Fe}_{0.3}$ with hydrogen interstitial at normal pressure.

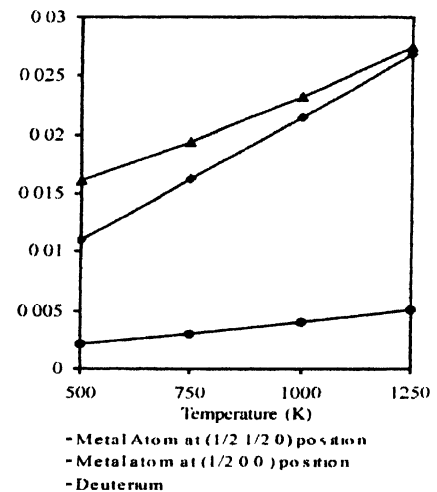


Figure 4. MSD of $\text{Cr}_{0.7}\text{Fe}_{0.3}$ with deuterium interstitial at normal pressure

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. The same trend has been observed and discussed in the case of Nb atoms in NbH_x [8–10]. Due to the heavier mass of ^2H , the MSD of surrounding atoms and ^2H is less than that of H interstitial. The decrease in MSD values with increase of pressure for both types of impurities is due to the shrinkage of the lattice. The same trend has been observed for the intermetallic compound $\text{Fe}_{0.5}\text{Ti}_{0.5}$ [11] and the substitutional alloy $\text{Ni}_{0.5}\text{Fe}_{0.5}$ [12].

The value of diffusion parameters obtained for the present system 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 for H. The result is compared with the available experimental data for diffusion of H in Fe-Cr alloy [13] 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 $Cr_{0.7}Fe_{0.3}$ is 1000 times greater than that of Cr-Fe system for a given temperature. In $Cr_{0.7}Fe_{0.3}$ 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 $E_{a,H} < E_{a,D}$ holds good. The isotope effect is similar to what was observed for diffusion of H in *bcc* metals like Nb and V and is consistent with the quantum tunneling diffusion nature [14,15]. In the low temperature region, the diffusivity

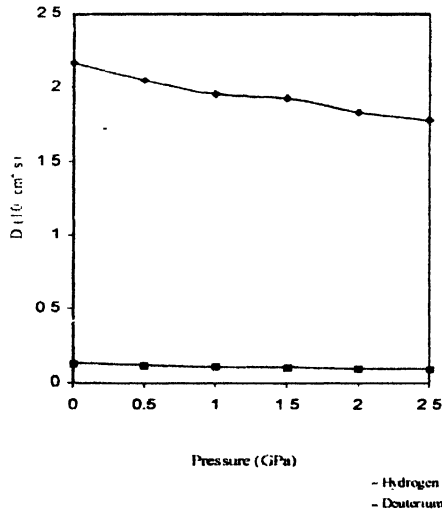


Figure 5. Diffusivity of H and 2H in $Cr_{0.7}Fe_{0.3}$ alloy as a function of pressure at the temperature of 500 K.

Appendix

The evaluated (3×3) dynamical matrix elements are given below :

$$D(1,1) = \frac{1}{m} [8A_1 \cos \pi q_x \cos \pi q_y \cos \pi q_z + 2A_2 \cos 2\pi q_x + 2B_2 (\cos 2\pi q_y + \cos 2\pi q_z) + 4A_3 (\cos 2\pi q_x \cos 2\pi q_y + \cos 2\pi q_x \cos 2\pi q_z)]$$

ratio D_{11}/D_{211} increases abruptly to the value of 18 and as reported earlier for some *bcc* metals [16], it approaches the value of $\sqrt{2}$ gradually in the high temperature region. Also the diffusivity ratio D_{11}/D_{211} is always greater than unity and it is temperature and pressure dependent as already mentioned by Alefeld and Volkl [14]. 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 5. A gradual decrease of diffusivity with increase in pressure indicates that, unlike $Ni_{0.5}Fe_{0.5}$ system [12], the present system of study $Cr_{0.7}Fe_{0.3}$ should be maintained at constant pressure while using it as storage medium.

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$$+ 4C_3 \cos 2\pi q_y \cos 2\pi q_z + 8A_4 \cos \pi q_x \times (\cos \pi q_y \cos 3\pi q_z + \cos 3\pi q_y \cos \pi q_z) + 8D_4 \cos 3\pi q_x \cos \pi q_y \cos \pi q_z + 8A_5 \cos 2\pi q_x \cos 2\pi q_y \cos 2\pi q_z + 2A_6 \cos 4\pi q_x + 2B_6 (\cos 4\pi q_y + \cos 4\pi q_z)],$$

$$\begin{aligned}
D(1,2) = & \frac{1}{m} [8B_1 \sin \pi q_x \sin \pi q_y \cos \pi q_z \\
& + 4B_3 \sin 2\pi q_x \sin 2\pi q_y \\
& + 8B_4 \sin \pi q_x \sin \pi q_y \cos 3\pi q_z \\
& + 8C_4 \cos \pi q_z (\sin 3\pi q_x \\
& \sin \pi q_y + \sin \pi q_x \sin 3\pi q_y) \\
& + 8B_5 \sin 2\pi q_x \sin 2\pi q_y \cos 2\pi q_z].
\end{aligned}$$

$$\begin{aligned}
D(1,3) = & \frac{1}{m} [8B_1 \sin \pi q_x \sin \pi q_z \cos \pi q_y \\
& + 4B_3 \sin 2\pi q_x \sin 2\pi q_z \\
& + 8B_4 \sin \pi q_x \sin \pi q_z \cos 3\pi q_y \\
& + 8C_4 \cos \pi q_y (\sin 3\pi q_x \\
& \sin \pi q_z + \sin \pi q_x \sin 3\pi q_z) \\
& + 8B_5 \sin 2\pi q_x \sin 2\pi q_z \cos 2\pi q_y].
\end{aligned}$$

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

$$\begin{aligned}
D(2,2) = & \frac{1}{m} [8A_1 \cos \pi q_x \cos \pi q_y \cos \pi q_z \\
& + 2A_2 \cos 2\pi q_y \\
& + 2B_2 (\cos 2\pi q_x + \cos 2\pi q_z) \\
& + 4A_3 (\cos 2\pi q_x \cos 2\pi q_y \\
& + \cos 2\pi q_y \cos 2\pi q_z) \\
& + 4C_3 \cos 2\pi q_x \cos 2\pi q_z \\
& + 8A_4 \cos \pi q_y (\cos \pi q_x \cos 3\pi q_z
\end{aligned}$$

$$\begin{aligned}
& + \cos 3\pi q_x \cos \pi q_z) \\
& + 8D_4 \cos 3\pi q_y \cos \pi q_x \cos \pi q_z \\
& + 8A_5 \cos 2\pi q_x \cos 2\pi q_y \\
& \cos 2\pi q_z + 2A_6 \cos 4\pi q_y \\
& + 2B_6 (\cos 4\pi q_x + \cos 4\pi q_z)].
\end{aligned}$$

$$\begin{aligned}
D(2,3) = & \frac{1}{m} [8B_1 \sin \pi q_y \sin \pi q_z \cos \pi q_x \\
& + 4B_3 \sin 2\pi q_y \sin 2\pi q_z \\
& + 8B_4 \sin \pi q_y \sin \pi q_z \cos 3\pi q_x \\
& + 8C_4 \cos \pi q_x (\sin 3\pi q_y \\
& \sin \pi q_z + \sin \pi q_y \sin 3\pi q_z) \\
& + 8B_5 \sin 2\pi q_y \sin 2\pi q_z \cos 2\pi q_x].
\end{aligned}$$

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

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

$$\begin{aligned}
D(3,3) = & \frac{1}{m} [8A_1 \cos \pi q_x \cos \pi q_y \cos \pi q_z + 2A_2 \cos 2\pi q \\
& + 2B_2 (\cos 2\pi q_x + \cos 2\pi q_y) \\
& + 4A_3 (\cos 2\pi q_z \cos 2\pi q_x + \cos 2\pi q_z \cos 2\pi q_y) \\
& + 4C_3 \cos 2\pi q_x \cos 2\pi q_y \\
& + 8A_4 \cos \pi q_z (\cos \pi q_x \cos 3\pi q_y \\
& + \cos 3\pi q_x \cos \pi q_y) + 8D_4 \cos 3\pi q_z \cos \pi q_x \cos \pi q_y \\
& + 8A_5 \cos 2\pi q_x \cos 2\pi q_y \cos 2\pi q_z + 2A_6 \cos 4\pi q \\
& + 2B_6 (\cos 4\pi q_x + \cos 4\pi q_y)].
\end{aligned}$$

where m is the atomic mass of the system and q_x , q_y and q_z are the x , y and z components of the wave vector, respectively.