

Atomic displacements due to interstitial hydrogen in Cu and Pd

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Abstract. The density functional theory (DFT) is used to study the atomic interactions in transition metal-based interstitial alloys. The strain field is calculated in the discrete lattice model using Kanzaki method. The total energy and hence atomic forces between interstitial hydrogen and transition metal hosts are calculated using DFT. The norm-conserving pseudopotentials for H, Cu and Pd are generated self-consistently. The dynamical matrices are evaluated considering interaction up to first nearest neighbors whereas impurity-induced forces are calculated with $M_{32}H$ shell (where $M = Cu$ and Pd). The atomic displacements produced by interstitial hydrogen at the octahedral site in Cu and Pd show displacements of 7.36% and 4.3% of the first nearest neighbors respectively. Both Cu and Pd lattices show lattice expansion due to the presence of hydrogen and the obtained average lattice expansion $\Delta V/V = 0.177$ for Cu and 0.145 for Pd.

Keywords. Atomic displacements; density functional theory; Kanzaki method.

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1. Introduction

The presence of point defect in a crystal, such as a vacancy or an impurity atom, generally causes a displacement of the neighboring host atoms from their ideal lattice positions. Such lattice distortions are measured using X-ray diffraction and more recently by X-ray absorption fine structure (EXAFS) experiments. Theoretically, the calculation of atomic displacements due to interstitial defects are difficult due to lack of appropriate interatomic potential in that distance range between long range interaction and short range potential. For the detailed understanding of metal–hydrogen system, information about the microscopic interaction between the interstitial hydrogen and the surrounding host-metal atoms is essential. However, in spite of much information accumulated in the literature, there are still open questions regarding the forces and the displacements of the nearest neighbors (NNs) of the interstitial hydrogen atom as interatomic potentials fail at the distance

where the interstitial atom occupies its position. The study of the interaction of interstitial hydrogen with Pd using first principle calculation, due to Elsasser *et al* [1] has helped in understanding the forces between the hydrogen and Pd atom and further the external force due to impurity atom in transition metals (TMs), could be calculated accurately from the total energy of the system using Hellmann–Feynman theorem [2]. This encourages us to study the interstitial alloys such as metal–hydrogen systems in detail using first principle calculations.

Total energy calculations and molecular dynamics simulations employing DFT are reliable tools for theoretical studies in condense matter physics and material science. A large number of their application in systems such as different molecules, bulk material and surfaces have proven the power of these methods in analyzing as well as predicting equilibrium and non-equilibrium properties. Self-consistent all-electron calculation of the total energy and electronic structure of the solids, are basis for carrying out the first principle computational calculations. The formalism due to Bockstedte *et al* [3] based on DFT, offers an accurate and efficient framework for treating the defects in TMs and the same has been used in the current work. In this formalism the calculation of total energy and the Kohn–Sham operator in a plane wave basis set is done by momentum space method [4]. The Kohn–Sham equations are solved using iterative schemes of Williams and Soler [5] and Payne *et al* [6]. The frozen core electrons are considered by norm-conserving pseudopotential in a fully separable form [7].

The aim of the present work is to study the TM-based interstitial alloys by calculating the interatomic forces due to interstitial hydrogen in TM host (Cu and Pd) using DFT, and subsequently use these forces to calculate the atomic displacements using discrete lattice static method [8–10]. The data obtained from these calculations are of vital importance to study the elastic and electronic properties of dilute alloys [11–13]. The plan of the paper is as follows: The theoretical methods, Kanzaki method and formalism to calculate external force using DFT, are described briefly in §2. The computational details of the calculation are described briefly in §3. The calculations and results are presented in §4 and are discussed in §5.

2. Theoretical methods

2.1 Kanzaki method

When an impurity is introduced in a perfect lattice, the lattice gets strained, and the host atoms move to new equilibrium positions $\vec{R}_n = \vec{R}_n^0 + \vec{u}(\vec{R}_n^0)$, where $\vec{u}(\vec{R}_n^0)$ are the atomic displacements. The potential energy of the strained lattice under applied external forces is expanded in power series of the displacements which in the harmonic approximation is given as

$$\Phi = \Phi_0 - \sum_{n,\alpha} u_\alpha(\vec{R}_n^0) F_\alpha(\vec{R}_n^0) + \frac{1}{2} \sum_{n,\alpha} \sum_{n',\beta} u_\alpha(\vec{R}_n^0) u_\beta(\vec{R}_{n'}^0) \phi_{\alpha\beta}(n, n'), \quad (1)$$

where Φ_0 is the potential energy of the perfect lattice, \vec{R}_n^0 is the equilibrium position of the n th host atom and $F_\alpha(\vec{R}_n^0)$ is the α component of the external force applied on

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the atom R_n^0 and $\phi_{\alpha\beta}(n, n')$ are the force constants which obey crystal symmetries. The equilibrium values of $u(R_n^0)$ are obtained by minimizing Φ with respect to $u_\alpha(R_n^0)$, which gives

$$F_\alpha(\vec{R}_n^0) = \sum_{n', \beta} \phi_{\alpha\beta}(n, n') u_\beta(\vec{R}_{n'}^0). \quad (2)$$

Evidently the displacements can be evaluated if $F_\alpha(\vec{R}_n^0)$ and $\phi_{\alpha\beta}(n, n')$ are known. In the Kanzaki lattice static method the displacements are expanded in normal co-ordinates as $u_\alpha(\vec{R}_n^0) = \sum_{\vec{q}} Q_\alpha(\vec{q}) \exp(i\vec{q} \cdot \vec{R}_n^0)$, where \vec{q} is a wave vector and the expansion coefficients $Q_\alpha(\vec{q})$ are normal co-ordinates known in dynamical theory. Since we are considering a periodic superlattice of defects, the wave vectors \vec{q} must satisfy periodic boundary conditions, and all such physically distinct \vec{q} vectors will be contained within the first Brillouin zone. $Q_\alpha(\vec{q})$ are in general, complex and, to ensure the reality condition for displacements, we must have $Q(-q) = Q^*(q)$, where the asterisk stands for the complex conjugate. Using $Q_\alpha(\vec{q})$, one gets the Fourier transform of the total energy Φ of the strained lattice as

$$\Phi = \Phi_0 - \sum_{\alpha q} F_\alpha(\vec{q}) Q_\alpha(\vec{q}) + \frac{N}{2} \sum_{\alpha\beta} \sum_q \phi_{\alpha\beta}(\vec{q}) Q_\alpha(\vec{q}) Q_\beta(\vec{q}), \quad (3)$$

where N is the number of lattice points in the crystal and $F_\alpha(\vec{q})$ and $\phi_{\alpha\beta}(\vec{q})$ are the Fourier transforms of $F_\alpha(\vec{R}_n^0)$ and $\phi_{\alpha\beta}(n - n')$, respectively. Using equilibrium condition in the Fourier space, eq. (3) gives

$$\sum_{\beta} [N \phi_{\alpha\beta}(-\vec{q}) Q_\beta(\vec{q}) - F_\beta(\vec{q}) \delta_{\alpha\beta} \delta_{-\vec{q}, \vec{q}}] = 0. \quad (4)$$

Equation (4) gives three simultaneous equations for three components $Q_\beta(q)$ for each value of q . If $\phi_{\alpha\beta}(q)$ and $F_\beta(q)$ are known, eq. (4) can be solved for $Q(q)$ which, in turn, gives $u_\alpha(\vec{R}_n^0)$.

In metallic crystals the ions are screened by the conduction electrons thereby decreasing the potential faster. It has been found that in d-band metals the screening is very heavy [14,15]. Therefore, major contribution to $\phi_{\alpha\beta}(\vec{q})$ and $F_\alpha(\vec{q})$ arises from the few NNs. Including the interactions up to 1NNs, $\phi_{\alpha\beta}(\vec{q})$ for fcc structure can be derived as described in [9,10]. Similarly, the external force due to interstitial impurity at octahedral site is obtained at the 1NN shell using the Fourier transforms of $F_\alpha(\vec{R}_n^0)$, for the interstitial impurity which gives

$$F_\alpha(q) = i2F_I \sin\left(\frac{q_\alpha a}{2}\right), \quad (5)$$

where F_I is the force acting on the 1NN site of the interstitial impurity. Similarly considering the 2NN's shell of the impurity, we get

$$F_\alpha(q) = i \frac{8}{\sqrt{3}} F_{II} \sin\left(\frac{q_\alpha a}{2}\right) \cos\left(\frac{q_\beta a}{2}\right) \cos\left(\frac{q_\gamma a}{2}\right), \quad (6)$$

where F_{II} is the force acting on the 2NN site of the interstitial impurity. With the knowledge of $\phi_{\alpha\beta}(\vec{q})$ and $F_{\alpha}(\vec{q})$, eq. (4) is solved for $\vec{Q}(\vec{q})$ for radial forces on the 1NNs and 2NNs of impurity. These values of $\vec{Q}(\vec{q})$ are used to calculate the atomic displacements. The sum is replaced by integration and $\vec{u}(\vec{R}_n^0)$ are calculated for different values of \vec{R}_n^0 using quadrature method for numerical integration.

2.2 Evaluation of external force

The external force exerted due to interstitial hydrogen in Cu and Pd are evaluated self-consistently from the total energy of the defect system (host lattice + impurity) in the DFT formalism. For a more accurate evaluation of interatomic forces, the quantum electronic structure of the system must be precisely known, which is obtained by solving the many-body Schrödinger equation for host-impurity system, which is given as

$$H_{\text{MB}} = \sum_{\mu} \frac{\hat{P}_{\mu}^2}{2M_{\mu}} + \sum_i \frac{\hat{p}_{\mu}^2}{2m} + \frac{1}{2} \sum_{ij} \frac{1}{|\vec{r}_i - \vec{r}_j|} - \sum_{\mu i} \frac{Z_{\mu}}{|\vec{r}_i - \vec{R}_{\mu}|} + \frac{1}{2} \sum_{\mu\nu} \frac{Z_{\mu}Z_{\nu}}{|\vec{R}_{\mu} - \vec{R}_{\nu}|}, \quad (7)$$

where Z_{μ} and M_{μ} are ionic charges and masses and \hat{P}_{μ} and \hat{p}_i are momentum operator for ions and electrons, m is the electron mass, r_i and R_{ν} are the electronic and atomic coordinates respectively. To solve eq. (7) rigorously, the electron and ionic motions are decoupled using Born–Oppenheimer approximation.

$$H_{\text{MB}} = \sum_{\mu} \frac{\hat{P}_{\mu}^2}{2M_{\mu}} + E(\{\vec{R}_{\mu}\}), \quad (8)$$

$$\left(H_{\text{MB}} - \sum_{\mu} \frac{\hat{P}_{\mu}^2}{2M_{\mu}} \right) \Psi_{\{\vec{R}_{\mu}\}}(\vec{r}_i) = E(\{\vec{R}_{\mu}\}) \Psi_{\{\vec{R}_{\mu}\}}(\vec{r}_i), \quad (9)$$

where $E(\{\vec{R}_{\mu}\})$ is the ground state energy of an electron system with frozen ionic coordinates $\{\vec{R}_{\mu}\}$ and $\Psi_{\{\vec{R}_{\mu}\}}(\{\vec{r}_i\})$ is the many-body electron wave function. The atomic forces can then be obtained from ground state energy using Hellmann–Feynman theorem (i.e. taking partial derivatives of $E(\{\vec{R}_{\mu}\})$) [2]

$$F_{\nu} = - \frac{\partial E(\{\vec{R}_{\mu}\})}{\partial \vec{R}_{\nu}}. \quad (10)$$

The calculation of the ground energy $E(\{\vec{R}_{\mu}\})$, as well as its derivative become more accurate and tractable with mean field theory approach using density functional theory (DFT). DFT methods are based on Hohenberg–Kohn theorem [16]. The total energy of the system is defined as

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$$E(\{\vec{R}_\mu\}) = E[\rho_{\text{gs}}(\vec{r})] + \frac{1}{2} \sum_{\mu,\nu} \frac{Z_\mu Z_\nu}{|\vec{R}_\mu - \vec{R}_\nu|}, \quad (11)$$

where the energy $E[\rho_{\text{gs}}(\vec{r})]$ represents the electronic part of the total energy $E(\{\vec{R}_\mu\})$ and second part represents the ionic part. Here instead of solving the true many-body eq. (9) in order to find $E(\{\vec{R}_\mu\})$, we only need to find a minimum of the functional $E[\rho]$. The ionic part of the total energy is evaluated using Coulombic interactions approximated by Ewald convergence method [17]. The cost of this great simplification is that we actually do not know the exact form of the functional $E[\rho]$. Nevertheless, this problem is solved by applying the method of Kohn and Sham [16]. In this method the electronic energy functional $E[\rho(\vec{r})]$ is split into four parts, i.e.

$$E[\rho] = T_e[\rho] + E_{\text{ion}}[\rho] + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho], \quad (12)$$

where $T_e[\rho]$ is the kinetic energy of electrons and $E_{\text{ion}}[\rho]$ is the energy of electron-ion interaction, i.e.

$$E_{\text{ion}}[\rho] = \int V_{\text{ion}}(r')\rho(r')dr', \quad V_{\text{ion}} = - \sum_{\mu} \frac{Z_\mu}{|\vec{r} - \vec{R}_\mu|}, \quad (13)$$

where V_{ion} is the electron-ion interaction potential, which is replaced by effective soft pseudopotential to enable efficient use of a plane-wave basis. The pseudopotential method [7] exploits the fact that for most of the atomic species the core electrons only weakly participate in the chemical bonding in the solid and thus their contributions can be approximated by smooth and slow varying potential, which increases the computational efficiency. $E_{\text{H}}[\rho]$ is the energy of classical Hartree electron-electron interaction given as

$$E_{\text{H}}[\rho] = \frac{1}{2} \int V_{\text{H}}(\vec{r})\rho(\vec{r})d\vec{r},$$

where Hartree potential

$$V_{\text{H}}(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}', \quad (14)$$

and finally E_{xc} is the term that accounts for electronic exchange and correlation effects. We can write a formal expression for an exchange-correlation potential using the functional derivative, i.e.

$$V_{\text{xc}}(\vec{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\rho(\vec{r})}. \quad (15)$$

$T_e[\rho]$ is the kinetic energy of a system of non-interacting electrons with electron-charge density equal to $\rho(\vec{r})$, i.e.

$$T_e(\rho) = 2 \sum_{i \text{ occ}} \left\langle \phi_i \left| -\frac{1}{2m} \nabla^2 \right| \phi_i \right\rangle, \quad (16)$$

where $\rho(r)=2\sum_{iocc}|\phi_i(r)|^2$ and $\phi_i(r)$ are the single electron orbitals. Now the variational principle can be used in eq. (12), since only the minimum value of Kohn–Sham energy functional has physical meaning. At the minimum, the Kohn–Sham energy functional is equal to the ground state energy of the system of electrons with ion positions $\{R_\nu\}$.

3. Computational details

For the calculation of total energy of a defect system, central quantities of interest are the ionic interaction V_{ion} and atomic arrangement of atoms in the system. The ionic interactions as described using eq. (13) are considered through norm-conserving pseudopotential in a fully separable form [7]. The exchange-correlation interactions are considered through GGA [18] while calculating the pseudopotential. The transferability of the pseudopotential is examined by examining scattering properties by taking logarithmic derivative at the core cut-off radius, and calculating the excitation energies of the free pseudoatom.

The ionic pseudopotentials for H, Cu, and Pd are generated using the *ab initio* method [7]. The hydrogen pseudopotential is calculated in scalar-relativistic mode, with number of valence states = 1 and $l_{max} = 1$. The core cut-off radius for hydrogen $r_{cut} = 0.78$ a.u. The variation of the ionic pseudopotential involving only s wave function shows minima at $r = 0.3$ a.u. and becomes nearly constant beyond $r = 5$ a.u. For Cu pseudopotential, we use $Z = 29.0$, valence electrons = 11, core states = 5, valence states = 2, $l_{max} = 3$ and core cut-off radius is fixed at $r_{cut} = 2.1$ a.u. The s -, p -components are small and nearly constant while d -component is strongly attractive and shows minima at about $r = 0.2$ a.u. Cu ionic pseudopotential becomes nearly constant for $r > 2$ a.u. For Pd pseudopotential calculation, we use $Z = 46.00$, valence electrons = 10, core states = 8, valence states = 2, $l_{max} = 3$ and $r_{cut} = 3.15$ a.u. It is interesting to note that the ionic pseudopotential for Pd is not the same as for Cu. The s -component has a minimum at $r = 1.5$ a.u., while p -component is increasing steadily. The d -component has the broad minima at $r = 0.7$ a.u. and the potential becomes constant at large distance. The pseudopotential for Pd ions is weaker than the Cu ion. The pseudopotential for Cu is short-ranged as components to the pseudopotential for hydrogen and Pd ion. Interestingly the hydrogen pseudopotential is feeble but long-ranged and extending its effect for the distant host atom.

For electronic structure calculations, the geometry of the atomic arrangement in the system (interstitial hydrogen in fcc lattice) is defined through structure factor. We consider the cluster of $M_{32}H$ shell (where $M = Cu$ and Pd) for total energy calculation using eq. (7). For solving eq. (7), we use the computational procedure developed by Bockstedte *et al* [3]. The exchange-correlation energy are evaluated using GGA with the same set of parameters as used to generate pseudopotential [18].

The initial wave functions $|\phi_{i,k}^0\rangle$ are calculated by explicit diagonalization of the the Kohn–Sham operator in the mixed basis set. After each iteration step the wave function $|\phi_{ik}\rangle$ is ortho-normalized by Gram–Schmidt scheme. We use energy cut-off limit for plane waves as $E_{cut} = 12$ Ry and for the initial wave function the energy

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Table 1. Some physical parameters (in a.u.) for Cu and Pd. a is the lattice constant, Z is the number of electrons in the outer orbit, and A_1 and B_1 are force constants for Cu and Pd. F_I and F_{II} (a.u.) are hydrogen-induced forces at the first and second nearest neighbors.

Host	a	Z	A_1	B_1	F_I	F_{II}
Cu	6.82	11	0.01567	-0.0035	0.0269	0.0013
Pd	7.35	10	0.0400	-0.0094	0.0372	0.0025

cut-off is $E_{\text{cut}} = 8$ Ry. The damped Joannopoulos algorithm [19,20] is used for wave function iteration to minimize the energy of the system, and obtain convergence. The interatomic forces are calculated using eq. (10) at the atomic site. Since atomic displacements due to interstitial hydrogen are calculated using Kanzaki method, the atomic forces are required at the fixed lattice points. Therefore, lattice is not allowed to relax, i.e. the positions of the atoms are kept fixed while calculating the forces at the required positions.

4. Calculations and results

We have used theoretical methods described in §2 to calculate the lattice distortion produced by interstitial hydrogen in Cu and Pd. The quantity of central interest in evaluating the strain field due to interstitial hydrogen is the interatomic forces between a hydrogen atom and the surrounding host metal. In the present work, the forces calculated from total energy calculation using DFT are presented in table 1. The force constants A_1 and B_1 defined in [8,9] are also used in the present calculations and are given in table 1. The norm-conserving pseudopotential in fully separable form is used for calculating the total energy of the metal-hydrogen system, the computational details for which are explained in brief in §3.

These calculated values of F_I , F_{II} , A_1 and B_1 are used to calculate $\phi_{\alpha\beta}(\vec{q})$ and hence $\vec{Q}(\vec{q})$, with the help of eq. (4). The inverse Fourier transform of $\vec{Q}(\vec{q})$ gives $\vec{u}(\vec{R}_n^0)$. The numerical calculations are simplified if we integrate over the cube of edge $4\pi/a$ which inscribes the first Brillouin zone (BZ) and using the fact that, for any function $F(q)$

$$\int_{\text{BZ}} F(q) dq = \frac{1}{2} \int_{\text{cube}} F(q) dq \quad (17)$$

for fcc structures. The integration is carried out by the Gaussian quadrature method.

The atomic displacements of 22NNs due to interstitial hydrogen at octahedral site in Cu and Pd are given in tables 2 and 3. The nature of the atomic displacements of NNs for Cu and Pd is the same. The first 4NNs of hydrogen move away from the hydrogen, and fifth NNs show contraction towards the hydrogen atom. Then again next 4NNs move away from hydrogen and fifth towards hydrogen. Over all only few NNs move towards the impurity and most of them move away from the impurity

Table 2. Atomic displacements (a.u.) of the NNs of hydrogen at octahedral site in the Cu metal. (n_1, n_2, n_3) (in $\frac{a}{2}$ units) are coordinates of the NNs and (u_x, u_y, u_z) are the Cartesian components of the atomic displacement.

(n_1, n_2, n_3)	u_x	u_y	u_z	$ u $
100	0.3552	0.0000	0.0000	0.3552
111	0.0159	0.0159	0.0159	0.0275
210	0.0554	0.0699	0.0000	0.0891
221	0.0270	0.0270	0.0294	0.0482
300	-0.0391	0.0000	0.0000	0.0391
311	0.0106	0.0214	0.0214	0.0321
320	0.0219	0.0328	0.0000	0.0394
331	0.0206	0.0206	0.0144	0.0325
333	0.0214	0.0214	0.0214	0.0371
410	-0.0232	-0.0004	0.0000	0.0233
421	0.0051	0.0130	0.0069	0.0155
430	0.0122	0.0182	0.0000	0.0219
432	0.0164	0.0171	0.0129	0.0270
441	-0.0017	-0.0017	-0.0011	0.0031
443	0.0146	0.0146	0.0060	0.0215
520	0.0160	0.0160	0.0000	0.0264
522	-0.0114	-0.0005	-0.0005	0.0114
533	0.0030	0.0043	0.0043	0.0061
540	0.0102	0.0099	0.0000	0.0173
544	0.0086	0.0117	0.0117	0.0145
630	0.0122	0.0109	0.0000	0.0196
641	-0.0058	0.0004	0.0001	0.0059

atom, and therefore lattice shows expansion. The displacements are oscillatory in nature but decreasing in magnitude with increase in the NNs distance. The maximum displacement is at 1NNs of hydrogen and Cu atoms are displaced more than Pd atoms. The maximum displacement of 7.36% and 4.3% of 1NN distance is found at the 1NNs of hydrogen in Cu and Pd respectively in our calculation as these atomic displacements are significant up to the first few NNs only. Thus hydrogen causes significant lattice expansion due to its interstitial location. The volume change is calculated considering the displacements up to 2NNs of the hydrogen atom. The calculated fractional relative change in the volume ($\Delta V/V$) is 0.177 and 0.145 for CuH and PdH systems. The experimental value of fractional change in volume for PdH system are found in the range of 0.20 to 0.13 for different concentrations of hydrogen in Pd, with average value 0.19 ± 0.01 [19,20]. However, the volume change may be estimated from Elsasser *et al* [1] results for the trace of the dipole tensor and the bulk modulus of Pd. For Pd_{32}H , $\text{Tr P} = 7.0$ eV and $\Delta V/V$ for H at the octahedral site is 0.134, which is close to the one calculated in this paper. These numbers are in reasonable qualitative agreement.

The calculated atomic displacements up to 2NNs are used to calculate the impurity-induced relaxation energy E_r which is given as

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Table 3. Atomic displacements (a.u.) of the NNs of hydrogen at octahedral site in the Pd metal. (n_1, n_2, n_3) (in $\frac{a}{2}$ units) are coordinates of the NNs and (u_x, u_y, u_z) are the Cartesian components of the atomic displacement.

(n_1, n_2, n_3)	u_x	u_y	u_z	$ u $
100	0.2254	0.0000	0.0000	0.2254
111	0.0104	0.0104	0.0104	0.0180
210	0.0355	0.0340	0.0000	0.0491
221	0.0125	0.0125	0.0111	0.0208
300	-0.0021	0.0000	0.0000	0.0021
311	0.0113	0.0086	0.0086	0.0166
320	0.0131	0.0145	0.0000	0.0195
331	0.0085	0.0085	0.0049	0.0129
333	0.0066	0.0066	0.0066	0.0114
410	-0.0004	0.0019	0.0000	0.0020
421	0.0058	0.0057	0.0031	0.0087
430	0.0066	0.0072	0.0000	0.0098
432	0.0061	0.0057	0.0044	0.0094
441	-0.0005	-0.0005	-0.0002	0.0007
443	0.0053	0.0053	0.0021	0.0078
520	0.0047	0.0047	0.0000	0.0077
522	0.0007	0.0019	0.0019	0.0021
533	0.0032	0.0026	0.0026	0.0048
540	0.0042	0.0032	0.0000	0.0062
544	0.0039	0.0040	0.0040	0.0056
630	0.0035	0.0029	0.0000	0.0054
641	0.0012	0.0014	0.0002	0.0018

$$E_r = -\frac{1}{2} \sum_{n\alpha} F_{n\alpha} u_{n\alpha}. \quad (18)$$

In the present calculation \vec{F} is isotropic and tabulated values of F_I, F_{II} in table 1 and the components of 1NN and 2NNs displacements from table 2 are used. The relaxation energy due to interstitial hydrogen in Cu is -0.076 eV and that in Pd is -0.067 eV. Therefore, hydrogen may be relatively easily mixed in Pd than in Cu which is in accordance with the experimental fact that hydrogen is less soluble in Cu than in Pd at similar conditions.

5. Discussion

The interstitial alloys are unique and the strain field due to these defects has been constrained due to non-availability of reliable interatomic potential at host-interstitial distance. The DFT provided a reliable method for calculating total energy and hence the atomic forces. Here the exchange and correlation effects of electrons are included explicitly and calculated self-consistently using GGA. The norm-conserving ionic pseudopotentials are generated in separable form, in total

energy calculation of the system. The transferability of the pseudopotential has been examined by examining scattering properties, excitation energies and chemical hardness properties of the free pseudoatom.

In the numerical calculations the cubic symmetry of the lattice is retained although the exact anisotropy of the Brillouin zone is not accounted for. This may not introduce serious error considering other simplifications in the calculations. Here we considered $M_{32}H$ shell ($M = \text{Cu}$ and Pd) due to our computational limitations. However, increasing the size of the shell may not influence the results to a large extent as major contribution in evaluating the interatomic forces is expected from only a few nearest neighbors. As the effective pseudopotential is extended up to $r = 5.0$ a.u., the considerations of forces up to 2NNs do not introduce any serious error. The cluster considered is not allowed to relax, i.e. fixed coordinates, and this is in accordance with our formalism to calculate strain field, as we require forces at fixed atomic sites. The reasonable agreement of the fractional volume change calculated from tabulated displacements and the experimental value shows that the interaction of the interstitial defects in alloys are effectively described using DFT. And the discrepancies in the results may be due to approximations considered in the discrete lattice static method (Kanzaki method).

The large displacements caused by the interstitial hydrogen in Cu and Pd need careful investigation, before considering technological use of such interstitial alloys in hydrogen environment. The hydrogen storage devices can be another technological applications of such hydrogenated systems. Further, the calculated displacements are of vital importance for the calculation of electric field gradient, heat of solution, Knight shift and other important physical properties where displaced positions of Cu and Pd atoms due to hydrogen are needed.

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