# Three-body effect on the lattice dynamics of Pd–10% Fe alloys

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We have developed a three-body potential based on a two-body model potential and applied it, as an application, to reproduce the experimental phonon frequencies of the fcc Pd–10% Fe alloy. For this purpose two- and three-body interactions have been employed to develop the dynamical matrix of the fcc structure. The parameters defining the two- and three-body potentials for Pd and Fe have been evaluated for the fcc structure at the lattice constant of the alloy. The radial, tangential, and three-body force constants of the alloy have been calculated by the concentration averages of the computed force constants of the component metals. Finally, the phonon frequencies of the alloy along the principal symmetry directions have been computed using the calculated force constants. The theoretical results are in good agreement with the corresponding experimental values.

## I. INTRODUCTION

There has been growing interest in the development of empirical and semiempirical interatomic potentials for more than thirty years, to investigate the elastic, lattice, and electronic properties of metals and alloys. The works in this field have also sustained the continued interest. Recently a two-body potential has been developed by Singh and Rathore[1] and it has been tested for phonon dispersion curves of fcc Fe. In this study, the cohesive energy, lattice constant, and compressibility are the input data for the model potential. As we know, compressibility and cohesive energy are the sum of the ionic interaction and the interaction due to electrons. For this purpose, i.e., to include the most significant contribution to the binding energy, which arises from the interaction between the metal ions and electrons, we have developed a three-body potential based on the two-body model potential of Ref. 1. The functional form and the parametrization procedure of the proposed three-body potential are explained in Sec. II B.

The interesting feature of Pd-Fe alloys is that the two constituents of the alloy are in different phases, as Fe is in the bcc phase and Pd in the fcc phase at room temperature. However, the Pd-Fe alloys form a random solution having a fcc structure.[2] Due to their structural complexity, not much theoretical work has been done on Pd-Fe alloys to reveal the lattice dynamics. Therefore the purpose of the present work is to investigate the suitability of applying both the two-body potential[1] and the three-body potential described in Sec. II B to the problem of studying the lattice dynamics of the Pd–10% Fe alloy.

## II. THEORY AND COMPUTATION

### A. Two-body model potential

If the interatomic interactions between two atoms of a lattice are of the model potential type developed by Singh and Rathore,[1] then the average interaction energy per atom may be written as

$$\phi_2(r)=\sum_j \frac{D}{2(m-1)r_j}[\beta^m\exp(-m\alpha r_j) - m\beta\exp(-\alpha r_j)] , \quad (1)$$

where $D$ is the dissociation energy of the pair, $\alpha$ is the constant which measures the hardness of the potential, $m$ is an exponent which delivers the same effect to the potential as results from the exchange and correlation effects due to electrons, $r_0$ is the separation of the atoms for minimum potential, and $\beta=\exp(\alpha r_0)$. In Eq. (1) the term $r_j^{-1}$ modifies the potential to exhibit the correct nature of the forces, particularly at small distances. The distance of the $j$th atom from the origin $r_j=a(m_j^2+n_j^2+l_j^2)^{1/2}$, where $m_j,n_j,l_j$ are integers representing the coordinates of the $j$th atom of the lattice and $a$ is the lattice constant.

The parameters $(\alpha,r_0,D)$ defining the model potential (1) for Pd and Fe are computed for the fcc structure at the lattice constant of the Pd–10% Fe alloy, following a similar method to the procedure given by Girifalco and Weizer.[3] The lattice constant of the alloy[2] is $a=0.38720$ nm. At equilibrium semilattice constant of the alloy, $a_0$,

$$\phi_2(r)|_{r=a_0}=\epsilon_0 ,$$
$$\left.\frac{d\phi_2(r)}{dr}\right|_{r=a_0}=0 , \quad (2)$$
$$\left.\frac{d^2\phi_2(r)}{dr^2}\right|_{r=a_0}=k ,$$

where $\epsilon_0$ is the pair energy at equilibrium, i.e., $\epsilon_0$ is the ionic part of the cohesive energy, and $k$ is the force constant at equilibrium. These parameters $(\epsilon_0,k)$ are available in the literature for most metals. For Fe and Pd the input data used in Eqs. (2) are given in Table I, where $\phi$ is the total cohesive energy.

Eight forms of the model potential (1) obtained by varying the exponent $m$ as 1.01, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 5.0 are studied for Pd and Fe, i.e., the potential pa-

 

TABLE I. Input data for Pd and Fe from Refs. 4–6.

| Element | $-\epsilon_0$ (eV) | $k$ (eV/nm$^2$) | $-\phi$ (eV) |
|---|---|---|---|
| Pd | 1.10 | 2315 | 3.89 |
| Fe | 0.90 | 926 | 4.28 |

rameters $(D,\alpha,r_0)$ are evaluated for each value of $m$ separately. In order to determine the best values of the exponent $m$ defining the two-body potential (1) for the elements we have then computed the elastic constants $(C_{11},C_{12},C_{44})$ for the fcc structure at the lattice constant of the alloy. The elastic constants can be evaluated from the well-known expressions for cubic crystals with two-body interatomic interactions:[7,8]

$$C_{11}=(a^4/2V)\sum_j m_j^4 D_j^2\phi_2(r_j)\ ,$$
$$C_{12}=(a^4/2V)\sum_j m_j^2 n_j^2 D_j^2\phi_2(r_j)\ , \tag{3}$$
$$C_{44}=\tfrac{1}{3}(2C_{11}-C_{12})\ ,$$

where $D_j=(1/r_j)(d/dr_j)$ and $V$ is the volume per atom. These relations are applicable to unstressed crystals only, i.e., the crystal must be in equilibrium with no external force applied. For $C_{44}$, the theoretical expression developed by Milstein and Rasky[8] is used because they have noted that the relations in Eqs. (3) are in better agreement with experimental data than the Cauchy relation $C_{44}=C_{12}$ for fcc crystals. Also, using the theoretical expression $C_{44}=\frac{1}{3}(2C_{11}-C_{12})$, the elastic constants of the fcc Fe–35% Ni alloy have been computed by Akgün,[17] and it is seen that the results obtained provide theoretical support for the efficacy of this relation in the fcc alloys. Thus the elastic constants of Pd and Fe at the lattice constant of the Pd–10% Fe alloy are calculated separately from Eqs. (3) for the values $m$ given above. Comparing the calculated values with experimental values of the elastic constants we have determined the values $m$ given in Table II for Pd and Fe. For Pd, the values of elastic constants obtained using the Linhard-Taylor[18] dielectric function are also given in Table II for comparison. For the determined values of the exponent $m$, the computed parameters $(\alpha,r_0,D)$ of the two-body potential (1) are given in Table III. In the computations we have considered couplings extending to the eighth neighbor of the fcc structure.

### B. Three-body potential

The total interaction energy of a system of $N$ atoms, in general, may be expressed as a many-body expansion,

TABLE III. Computed parameters for Pd and Fe at the lattice constant of the alloy.

| Element | $m$ | $D$ ($10^{-29}$ J m) | $\alpha$ ($10^{10}$ m$^{-1}$) | $r_0$ ($10^{-10}$ m) |
|---|---|---|---|---|
| Pd | 2.5 | 7.664 29 | 2.417 86 | 2.773 23 |
| Fe | 3.5 | 6.198 54 | 2.167 35 | 2.770 34 |

$$\phi=\phi_2+\phi_3+\cdots+\phi_n+\cdots\ , \tag{4}$$

where $\phi_2$, $\phi_3$, and $\phi_n$ represent the total two-body, three-body, and $n$-body interaction energies, respectively. Here we propose a three-body potential based on the two-body model potential (1). The three-body general potential coupling the atom $(l,k)$ with its two common nearest neighbors $(l',k')$ and $(l'',k'')$ may be written as

$$\phi_3(r_1r_2)=\sum_{l'k'\neq l''k''}\sum_{l,k}\frac{CD}{2(m-1)(r_1+r_2)}\times\{\beta^m\exp[-m\alpha(r_1+r_2)]-m\beta\exp[-\alpha(r_1+r_2)]\}\ , \tag{5}$$

where $r_1$ and $r_2$ are the respective separations of the atoms $(l',k')$ and $(l'',k'')$ from the atom $(l,k)$. $C$ is the only parameter in the three-body potential to be evaluated. The three-body potential parameter, $C$, can be evaluated easily by fitting the total interaction energy of an atom in a particular crystal structure to the total cohesive energy $\phi$ of the element. One can write the total interaction energy simply by separating $C$ as

$$\phi=\phi_2+C\phi_3\ . \tag{6}$$

For Pd and Fe, the necessary parameters used in the calculations are given in Tables I and III. In the calculation of the lattice sums in $\phi_2$ given by Eq. (1) we have considered the two-body couplings extended to the eighth neighbor of the fcc structure. For the three-body interaction considered here, the first neighbor of the fcc configuration is regarded as the common nearest neighbor of the second and third neighbors. Therefore the computed values of the three-body potential parameter at the lattice constant of the alloy Pd–10% Fe are $C=27.1474$ for Pd and $C=24.4989$ for Fe.

### C. Phonon dispersion relations

In the harmonic and adiabatic approximations, the phonon frequencies corresponding to a wave vector $\mathbf{k}$ for a cubic crystal are determined by solving the secular equation, given by

$$|D-MW^2I|=0\ , \tag{7}$$

TABLE II. Computed elastic constants (in units of $10^{11}$ N/m$^2$) for Pd and Fe at room temperature.

| Pd | | | | Fe | | | | |
|---|---|---|---|---|---|---|---|---|
| $m$ | $C_{11}$ | $C_{12}$ | $C_{44}$ | $m$ | $C_{11}$ | $C_{12}$ | $C_{44}$ | Ref. |
| 2.5 | 2.61 | 1.40 | 1.27 | 3.5 | 2.45 | 1.29 | 1.20 | Present work |
| | 2.27 | 1.76 | 0.71 | | 2.30 | 1.35 | 1.17 | Expt. (Refs. 9, 10) |
| | 1.70 | 1.33 | 1.14 | | | | | Theory (Ref. 18) |

where $D$ is the dynamical matrix of order $(3\times3)$, $I$ is the unit matrix, and $M$ is the ionic mass. In the present work, the elements of the dynamical matrix $D_{\alpha\beta}$ are composed of two-body ($D^i_{\alpha\beta}$) and three-body ($D^m_{\alpha\beta}$) parts:

$$D_{\alpha\beta}=D^i_{\alpha\beta}+D^m_{\alpha\beta} . \tag{8}$$

In the case of the two-body central pairwise potential, the interactions are assumed to be effective up to eighth nearest neighbors and the $D^i_{\alpha\beta}$ are evaluated by the scheme of Shyam, Upadhyaya, and Upadhyaya.[11] The typical diagonal and off-diagonal matrix elements of $D^i_{\alpha\beta}$ can be found in Ref. 11. In the case of the central interaction, first and second derivatives of the two-body potential $\phi_2(r)$ provide two independent force constants, i.e., the radial force constant $\alpha_i$ and tangential force constant $\beta_i$, for the $i$th set of neighbors:

$$\beta_i=\frac{1}{r}\frac{d\phi_2(r)}{dr}\bigg|_{r=r_i} ,$$
$$\alpha_i=\frac{d^2\phi_2(r)}{dr^2}\bigg|_{r=r_i} , \quad i=1-8 . \tag{9}$$

For Pd and Fe, the calculations of $\alpha_i$ and $\beta_i$ are done for the fcc structure at the lattice constant of the alloy Pd–10% Fe. Now we evaluate the force constants ($\alpha_i$ and $\beta_i$) of the alloy by using the linear relations

$$\alpha_i(\text{Pd-Fe})=(1-x)\alpha_i(\text{Pd})+x\alpha_i(\text{Fe}) ,$$
$$\beta_i(\text{Pd-Fe})=(1-x)\beta_i(\text{Pd})+x\beta_i(\text{Fe}) , \tag{10}$$

where $x$ is the concentration of Fe in the alloy ($x=0.10$). For Pd, Fe, and the Pd–10% Fe alloy the computed force constants are given in Table IV. The average mass used in the calculations for the alloy is obtained from the relation

$$M(\text{Pd-Fe})=(1-x)M(\text{Pd})+xM(\text{Fe}) . \tag{11}$$

In order to determine the contribution of the three-body forces to the diagonal and off-diagonal matrix elements of $D^m_{\alpha\beta}$, we follow the scheme of Mishra, Srivastava, and Mishra,[12] where a three-body empirical potential is used to deduce the force-constant matrix, involving a single parameter. For a fcc system, the elements of the diagonal and off-diagonal matrix may be given, after solving the usual secular determinant, as

$$D^m_{\alpha\alpha}=4\gamma[4-2C_{2i}-C_i(C_j+C_k)] ,$$
$$D^m_{\alpha\beta}=4\gamma[C_i(C_j+C_k)-2] , \tag{12}$$

where $\gamma$ is the second derivative of the three-body potential $\phi_3(r_1r_2)$, $C_i=\cos(\pi ak_i)$, and $C_{2i}=\cos(2\pi ak_i)$. To calculate the three-body force constant $\gamma$, we limit the short-range three-body forces in the fcc system only up to first nearest neighbors. For the alloy Pd–10% Fe, the three-body force constant is obtained from the linear relation

$$\gamma(\text{Pd-Fe})=(1-x)\gamma(\text{Pd})+x\gamma(\text{Fe}) . \tag{13}$$

The computed values of the three-body force constants at the lattice constant of the alloy are $\gamma=-625.001\times10^{-3}$ N m$^{-1}$ for Pd, $\gamma=-612.720\times10^{-3}$ N m$^{-1}$ for Fe, and $\gamma=-623.772\times10^{-3}$ N m$^{-1}$ for Pd–10% Fe.

Now one can construct the dynamical matrix $D_{\alpha\beta}$ by using Eq. (8) and then solve the secular equation (7) to compute the phonon frequencies along the principal symmetry directions [100], [110], and [111] for the alloy.

## III. RESULTS AND DISCUSSION

In the present paper, the interaction system of the fcc Pd–10% Fe alloy is considered to be composed of two-body and three-body parts. By a three-body interaction we mean an extra interaction energy owing to the presence of a third particle. This type of interaction may occur through the deformation of the electron shells.[13] The three-body potential (5) developed here and the two-body model potential (1) are used, as an application, to investigate the dynamical behavior of binary type-II alloys, where the end members have different structures. In the case of the two-body interaction, we have considered couplings extending to the eighth neighbor of the fcc structure. The parameters $(\alpha,r_0,D)$ defining the model potential $\phi_2(r)$ for pure Pd and Fe are evaluated for the fcc structure at the equilibrium lattice constant of the alloy, by knowledge of the equilibrium pair energies and the equilibrium force constants of the elements. The three-body parameter $C$ is evaluated from knowledge of the total cohesive energies (total interaction energies) of the elements. Thus, on one hand, we determine the *ab initio* radial and tangential force constants of Pd and Fe for the fcc structure at the lattice constant of the alloy by using the model potential (1) and, on the other, we reason-

TABLE IV. Computed radial ($\alpha_i$) and tangential ($\beta_i$) force constants for Pd–10% Fe.

| Serial no. | $\alpha_i$ ($10^{-3}$ N m$^{-1}$) Pd | Fe | Pd–10% Fe | $\beta_i$ ($10^{-3}$ N m$^{-1}$) Pd | Fe | Pd–10% Fe |
|---|---|---|---|---|---|---|
| 1 | 55 195.9 | 51 106.8 | 54 787.1 | −243.57 | −217.95 | −241.00 |
| 2 | −1 605.07 | −1 215.55 | −1 566.12 | 157.219 | 128.643 | 154.362 |
| 3 | −160.061 | −145.296 | −158.585 | 12.770 8 | 12.783 2 | 12.772 1 |
| 4 | −23.022 4 | −25.009 9 | −23.221 1 | 1.608 94 | 1.931 89 | 1.641 24 |
| 5 | −4.248 01 | −5.415 50 | −4.364 76 | 0.267 74 | 0.377 67 | 0.278 73 |
| 6 | −0.933 12 | −1.375 25 | −0.977 33 | 0.054 02 | 0.088 15 | 0.058 34 |
| 7 | −0.233 48 | −0.393 29 | −0.249 46 | 0.012 57 | 0.023 46 | 0.013 66 |
| 8 | −0.064 69 | −0.123 42 | −0.070 57 | 0.003 27 | 0.006 18 | 0.009 86 |

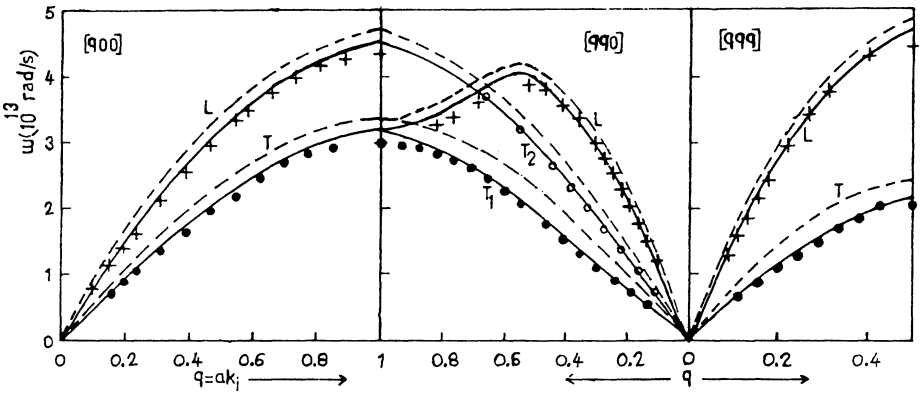


FIG. 1. Phonon dispersion curves at room temperature for Pd–10% Fe. The symbols (●, +, ○) represent the experimental values (Ref. 2). The solid curves show the dispersion curves computed by including the contribution of three-body forces and the dashed curves represent the computed dispersion curves according to the two-body central interactions.

ably account for the long-range character of interatomic forces by considering the interaction system extending up to eight sets of nearest neighbors. The three-body force constants of Pd and Fe are also calculated for the fcc structure at the lattice constant of the alloy, by using the three-body potential (5). In order to study the phonon dispersion relations of the alloy Pd–10% Fe, we calculate the radial, tangential, and three-body force constants of the alloy, using the concentration averages of the force constants of the constituent metals.

First, the phonon dispersion curves of the alloy are only computed according to the two-body central interaction and the results are shown by dashed curves in Fig. 1. Next the calculation is repeated for the alloy, by including the contribution of three-body forces to the dynamical matrix (8) and the computed dispersion curves are shown by solid curves in Fig. 1. Furthermore, the experimental values measured by Maliszewski *et al.*[2] for the alloy are also shown by the symbols (●, +, ○) in Fig. 1 for comparison. As seen from Fig. 1 the experimental and theoretical values are in good agreement when the three-body force is incorporated in the alloy. Also, all the calculations described in the text were repeated for the Pd–4% Fe alloy. As seen from the experimental findings[2] for the alloy, the computed dispersion curves are nearly identical to Fig. 1. Therefore the computed results for Pd–4% Fe are not given in this paper.

Recently, the radial and tangential force constants of Pd and Fe in the fcc phase have been computed by Singh, Banger, and Singh[14] and by Singh,[15] by including the contributions of *s* and *d* conduction electrons explicitly. In these calculations they have used a two-body pair potential defined as the sum of *s-s*, *d-d*, and *s-d* contributions.[14,15] The free-electron part of this pair potential was also obtained in second-order perturbation theory using the rational dielectric function and the empty-core pseudopotential.[14,15] Furthermore, Singh[16] has calculated the phonon frequencies of the alloys $Pd_{1-x}$ $Fe_x$ for the concentrations $x=0.04$ and 0.10, using the microscopic force constants obtained from the concentration averages of the force constants given in Refs. 14 and 15 for Pd and Fe in the fcc structure. He has noted that the discrepancies between theoretical and experimental results are found to be 11% and 10% for $x=0.04$ and 0.10, respectively. In this work[16] it is to be noted that the force constants of Pd and Fe are not evaluated by using the lattice constants of the alloys separately. In the present work, we have computed the radial, tangential, and three-body force constants of Pd and Fe separately, using the lattice constants of the alloys $Pd_{1-x}Fe_x$.

Consequently, for fcc binary type-II alloys the present results show that the proposed two- and three-body potentials are sufficient to reproduce the phonon data and the mean crystal model described above works well.

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