

Ab Initio Study of Structural, Electronic, and Thermal Properties of Pt/Pd-Based Alloys

Louise Magdalene Botha ^{1,*}, Cecil Naphtaly Moro Ouma ¹, Kingsley Onyebuchi Obodo ¹,
Dmitri Georgievich Bessarabov ^{1,*}, Denis Lvovich Sharypin ², Pyotr Sergeevich Varyushin ²
and Elizaveta Ivanovna Plastinina ²

- ¹ HySA-Infrastructure, Faculty of Engineering, North-West University,
Private Bag X6001, Potchefstroom 2520, South Africa;
moronaphtaly84@gmail.com (C.N.M.O.); obodokingsleyo@gmail.com (K.O.O.)
- ² PJSC MMC Norilsk Nickel, 15, 1st Krasnogvardeysky Drive, 123100 Moscow, Russia;
sharypindl@nornik.ru (D.L.S.); varyushinps@nornik.ru (P.S.V.);
plastininaei@nornik.ru (E.I.P.)
- * Correspondence: louise.botha@nwu.ac.za (L.M.B.);
dmitri.bessarabov@nwu.ac.za (D.G.B.)
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Corresponding author 1:

LM Botha,

e-mail address: Louise.Botha@nwu.ac.za

Corresponding author 2:

D.G. Bessarabov,

Telephone: +27 (0) 18 285 2460

e-mail address: Dmitri.Bessarabov@nwu.ac.za

Contents:

- Volume calculation for PtPd and Pt₇Pd alloy structures.
- Pair distribution function.
- VASP Input files: atomic coordinates (CONTCAR).
- VASP Input files: Settings (INCAR).
- VASP Input files: Molecular dynamics (INCAR).

1. Calculated lattice parameters.

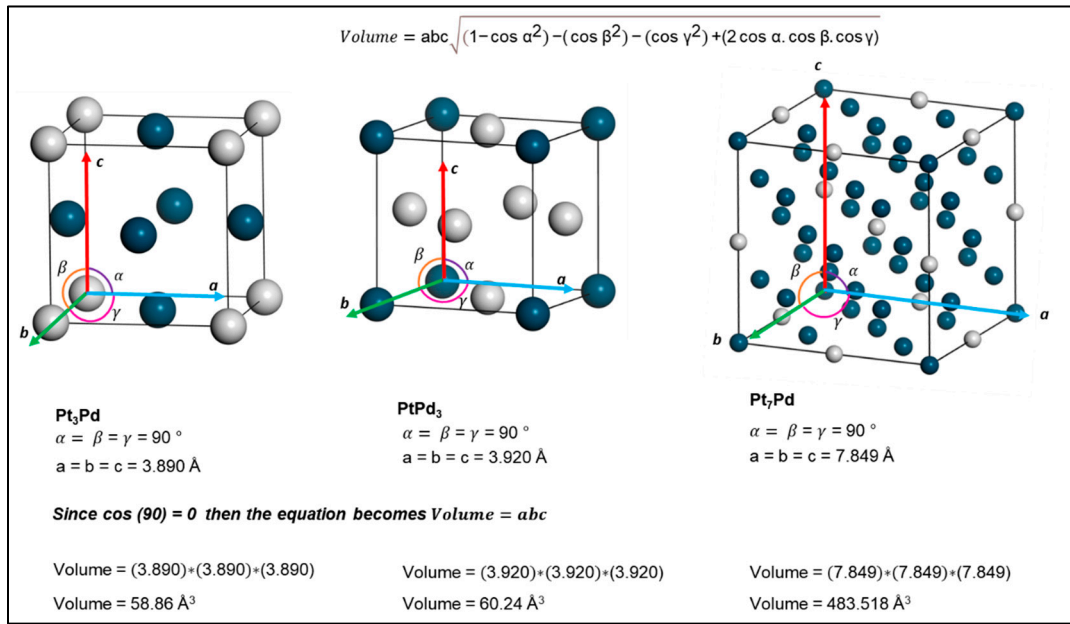


Figure S1. Volume calculation for cubic Pt/Pd alloy structures, where $\alpha = \beta = \gamma = 90^\circ$.

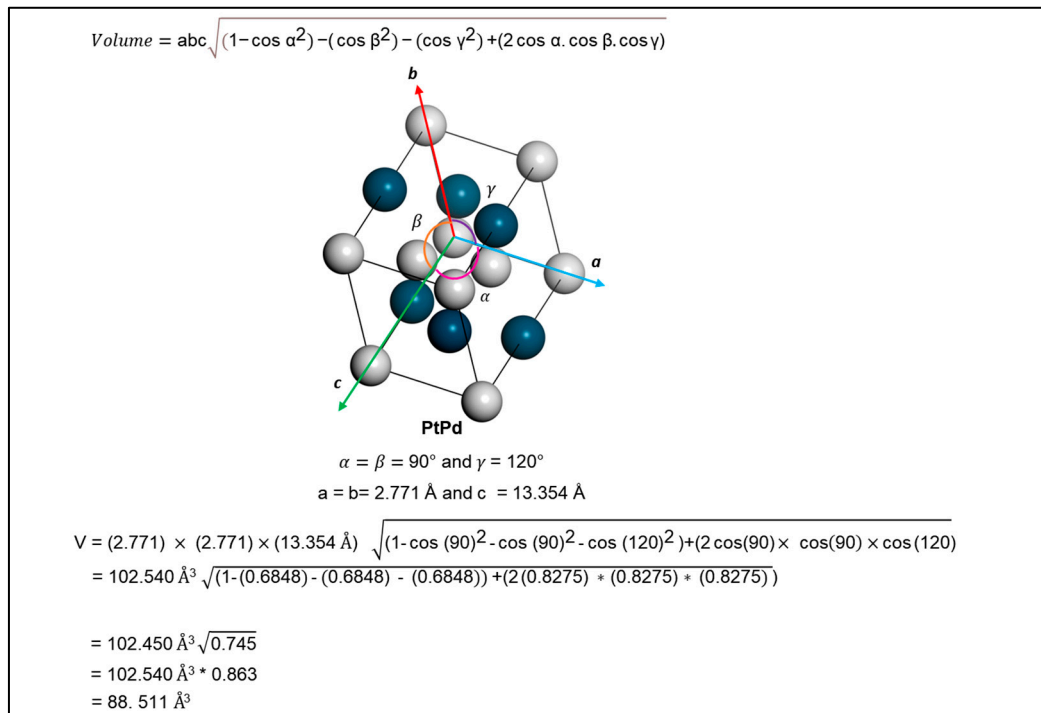


Figure S2. Volume calculation for non-cubic Pt/Pd alloy structure where $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$.

This structure presented above is rhombohedral-centred hexagonal with space group R 3M. Its volume is 88.80 \AA^3 , and the lattice parameters are $a = b = 2.771$ and $c = 13.354$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$. The PtPd structure was found to be stable, as indicated in Figure 1 of the manuscript.

2. Calculated Pair Distribution Function for Pt/Pd alloys

Molecular dynamics was performed using a kinetic energy cut-off fixed at 500 eV for the plane-wave basis set expansion of the Kohn–Sham (KS) valence states with an electronic convergence set at 10^{-5} eV. The Methfessel–Paxton approach was used with a smearing width of 0.2 eV. The $1 \times 1 \times 1$ Brillouin zones were sampled using Γ -centred Monkhorst-Pack grid. The micro-canonical ensemble (nVE) with changing temperature was selected. The simulation time was set to 100 fs with a timestep of 1.0 and a trajectory file frequency of 2. The thermal motions of the ions, presented in Figure S3, are characterised by the temperature evolution of the pair distribution function (PDF). The selected temperature range was 100–2100 K, which includes the melting temperature for Pt (2041 K) and Pd (1828 K).

Crystalline structures exhibit less diffuse pair correlation functions because the atoms vibrate around high symmetry points. In contrast, liquids have more diffuse pair correlation functions as the average positions of atoms are spread out over a wider range of distances. As the temperature decreases, the pair correlation function becomes more structured, reflecting the ordering of the atoms in a crystalline lattice, as shown in Figure S3. The calculated pair correlation function in the study showed that a high degree of dynamical stability is observed for the pristine Pt and Pd as well as the Pt/Pd alloy structures over a wide range of temperature.

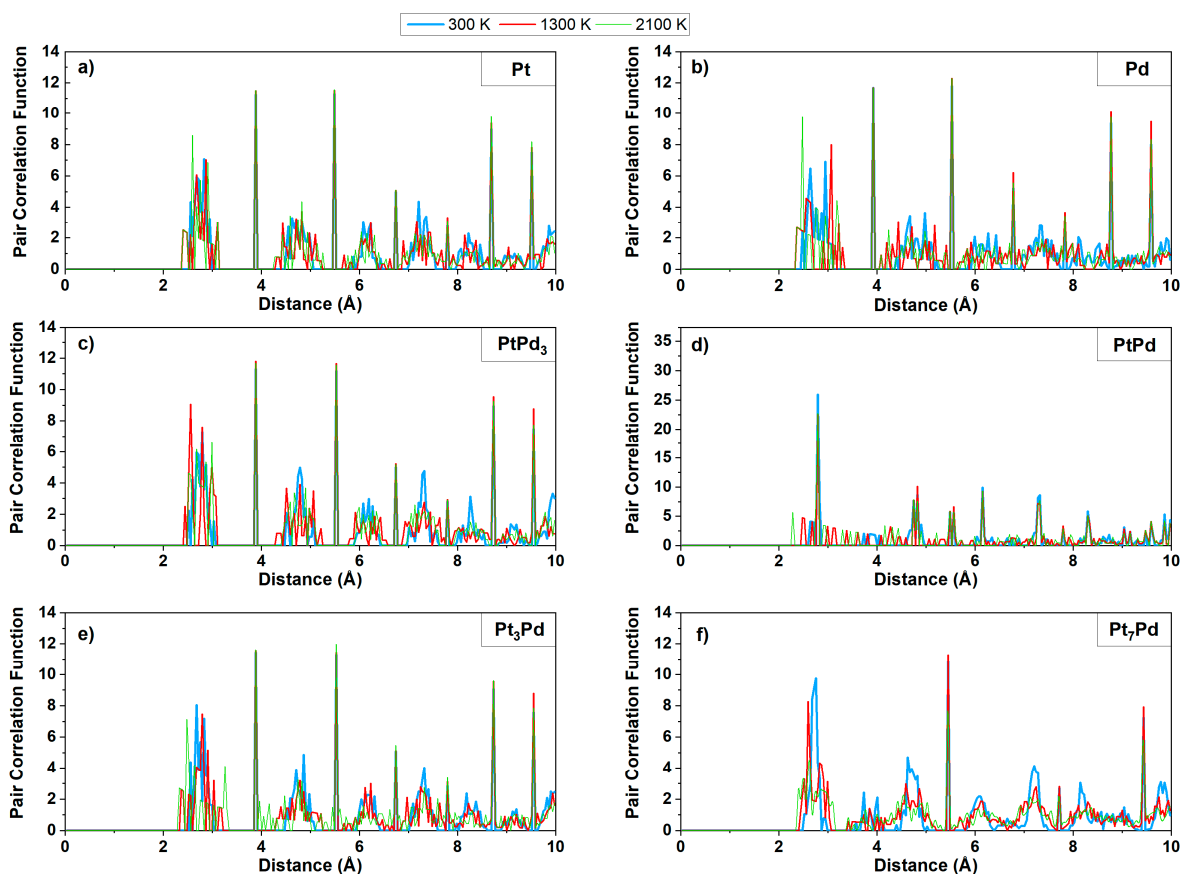


Figure S3. Temperature behaviour of the pair distribution function for the Pt-Pd bond distances, obtained from molecular dynamics (MD) simulations conducted over the range of 100K to 2100K. The plots represent the pristine structures of **a)** Pt, **b)** Pd, as well as the alloy structures for **c)** PtPd_3 , **d)** PtPd , **e)** Pt_3Pd and **f)** Pt_7Pd .

3. Mathematical equations and a comprehensive description of elastic properties.

This section includes a detailed explanation on the computation of the elastic constants (C_{ij}), bulk modulus (B), shear modulus (G), Young modulus (E), and Poisson (ν) ratio.

Elastic constants (C_{ij})

The elastic constant of a crystal structure is determined by deforming the unit cell as shown in (Eq. 1). This deformation is accomplished by using an engineering strain matrix e to change the Bravais lattice vectors $R = (a, b, c)$ of the undisturbed unit cell $R' = (a', b', c')$.

$$R' = R \begin{pmatrix} 1 + e_{xx} & \frac{1}{2}e_{xy} & \frac{1}{2}e_{xz} \\ \frac{1}{2}e_{yx} & 1 + e_{yy} & \frac{1}{2}e_{yz} \\ \frac{1}{2}e_{zx} & \frac{1}{2}e_{zy} & 1 + e_{zz} \end{pmatrix} \quad (\text{Eq. 1})$$

As a result of the deformation, the total energy of the energy changes, as shown in (eq. 2), where E_0 is the total energy of the unstrained lattice, V_0 is the volume of the undistorted cell, and C_{ij} are the elements of the elastic constant matrix with a notion that follows standard convention. The strain or stress is represented as a vector with six independent components, respectively, $1 \leq i, j \leq 6$, in the sequence (xx, yy, zz, yz, xz , and xy).

$$U = \frac{E_{tot} - E_0}{V_0} = \frac{1}{2} \sum_{i=1}^6 \sum_{j=1}^6 C_{ij} e_i e_j \quad (\text{Eq. 2})$$

The tensor of elasticity has 36 elements and the elastic constants, but maximally, 21 of these are independent ($C_{11}, C_{12}, C_{13}, \text{etc}$). The symmetry of the unit cell can reduce the number of independent elastic constants for the various symmetry systems, such as the cubic system, in which there are only three independent constants, C_{11}, C_{12} and C_{44} .

The elements of the stiffness matrix are then determined by the strain fields in (eq.1), which are applied to determine properties such as the bulk modulus, and the shear modulus, which represent the extreme limits of the elastic moduli.

Bulk modulus (B) and Shear modulus (G)

The bulk modulus (Eq. 3) provides a description of the elastic properties of a material since the material returns to its original volume once the pressure is released. As such, the bulk modulus is determined by the change in the pressure or force applied per unit area (ΔP), the change in the volume of the material due to compression (ΔV), and by the initial volume of the material (V).

$$B = \frac{\Delta P}{\Delta V/V} \quad (\text{Eq. 3})$$

Using the applied strain field ($e_{xx} = e_{yy} = e_{zz} = e$) allows for the computation of the bulk modulus, which responds to uniform compression, using the relationship (Eq. 4).

$$U = \frac{B e^2}{2} \quad (\text{Eq. 4})$$

The shear modulus is a response to shear stress or pressure in the xy direction (τ_{xy}) and shear strain (γ_{xy}), as shown in (Eq. 5).

$$G = \frac{\tau_{xy}}{\gamma_{xy}} \quad (\text{Eq. 5})$$

Similarly, to the bulk modulus, the shear modulus is calculated from the applied strain field, where the relationship is shown in (Eq. 6).

$$U = 3C' \frac{e^2}{2} \quad (\text{Eq. 6})$$

Overall, the stiffness matrix (C_{12}) is calculated using either of the relations shown in (Eq. 7 and Eq. 8).

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \quad (\text{Eq. 7})$$

$$C' = \frac{1}{2}(C_{11} - C_{12}) \quad (\text{Eq. 8})$$

Young's modulus (E) and Poisson's ratio (ν) are determined by the bulk modulus and the shear modulus.

Young modulus (E) and Poisson (ν) ratio.

The behaviour of the material towards bending/twisting deformation (stiffness) and the absolute ratio of the lateral strain (stretching and compression) in response to longitudinal strain are described using Young's modulus (Eq. 9) and Poisson's ratio (Eq.10).

In (Eq. 9) Young's modulus is determined by the uniaxial stress or uniaxial forces per unit surface (σ) and the strain, or the proportional deformation (ϵ).

$$E = \frac{\sigma}{\epsilon} \quad (\text{Eq. 9})$$

In (Eq. 10), Poisson's ratio is determined by the transverse strain ($d\epsilon_{trans}$) and the axial strain ($d\epsilon_{axial}$).

$$\nu = - \frac{d\epsilon_{trans}}{d\epsilon_{axial}} \quad (\text{Eq. 10})$$

Implementing computational methods, Young's modulus (E) and Poisson's ratio (ν) are determined by the previously calculated bulk modulus and shear modulus using (Eq. 11) and (Eq. 12).

$$E = \frac{9B}{1 + \frac{3B}{G}} \quad (\text{Eq. 11})$$

$$\nu = \frac{1}{2} \frac{B - \frac{2}{3}G}{2B + \frac{1}{3}G} \quad (\text{Eq. 12})$$

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- [1] Y. Le Page and P. Saxe, Symmetry-General Least-Squares Extraction of Elastic Coefficients From Ab Initio Total Energy Calculations, Phys. Rev. B **63**, 174103 (2001).
 - [2] Y. Le Page and P. Saxe, Symmetry-General Least-Squares Extraction of Elastic Data for Strained Materials From Ab Initio Calculations, of Stress, Phys. Rev. B **65**, 104104 (2002).
 - [3] O. L. Anderson, A Simplified Method for Calculating the Debye Temperature From Elastic Constants, J. Phys. Chem. Solids **24**, 909, (1963).

4. Mathematical equations and a comprehensive description of temperature properties.

Implementing the temperature to the elastic constants requires implementation of Grüneisen's theory [1], which is accomplished by evaluating the phonon spectra and the derivatives of the individual phonon frequencies.

Debye temperature (θ_D) and constant volume specific heat (C_v)

The Debye temperature is obtained from the number of atoms in the unit cell (q), the volume of the unit cell (V_0), the Planck and Boltzmann constants (h and k_B), and the sound velocity (v_m). Similarly, the sound velocity is determined by the mean values for the transverse (v_t) and longitudinal (v_l) sound velocities, which are given in terms of elastic moduli and the mean density (ρ) in equations (Eq. 15) and (Eq. 16).

$$\theta_D = \frac{h}{k_B} \left(\frac{6\pi^2 q}{V_0} \right)^{\frac{1}{3}} v_m \quad (\text{Eq. 13})$$

$$v_m = \left(\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right) \quad (\text{Eq. 14})$$

$$v_t = \sqrt{\frac{G}{\rho}} \quad (\text{Eq. 15})$$

$$v_l = \sqrt{\frac{B + \frac{4}{3}}{\rho}} \quad (\text{Eq. 16})$$

The contribution of the lattice to the specific heat capacity, C_v , as a function of temperature, T , can then be calculated using (Eq. 17).

$$C_v(T) = 9qk_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} x^4 \frac{e^x}{(e^x - 1)^2} dx \quad (\text{Eq. 17})$$

[1] E. Grüneisen's, Zustand des festen Körpers, in: Thermische Eigenschaften der Stoffe, Handbuch Der Physik, (Springer Berlin, Heidelberg, 1928).

[2] B Mayer, H Anton, E Bott, M Methfessel, J Sticht, J. Harris, and P. C. Schmidt, Ab-Initio Calculation of the Elastic Constants and Thermal Expansion Coefficients of Laves Phases, Intermetallics 11, 23 (2003).

5. VASP input files

This section includes the VASP input files required for each of the calculations. First, the atomic coordinates of the already optimised bulks are given, followed by the input files required for geometric optimisation, electronic properties, elastic constants, and phonopy band structures files.

5.1. Geometric Optimisation Input files

Table S1. Atomic coordinates of the Pt/Pd alloy structures, as implemented in VASP.

Alloy structure	VASP atomic coordinate files (CONTCAR)
PtPd ₃	1.000
	3.890 0.000 0.000
	0.000 3.890 0.000
	0.000 0.000 3.890
	Pt Pd
	1 3
	Direct
	0.000 0.000 0.000
	0.500 0.500 0.000
	0.500 0.000 0.500
PtPd	0.000 0.500 0.500
	1.000
	4.730 0.000 0.000
	3.918 2.650 0.000
	3.918 1.200 2.362
	Pt Pd
	1 1
	Direct
	0.500 0.500 0.500
	0.000 0.000 0.000
PtPd L1 ₀	1.0000
	3.899 0.000 0.000
	0.000 3.901 0.000
	0.000 0.000 3.901
	Pt Pd
	2 2
	Direct
	0.500 0.0000 0.5000
	0.500 0.5000 0.0000
	0.000 0.0000 0.0000
Pt ₃ Pd	0.000 0.5000 0.5000
	1.000
	3.920 0.000 0.000
	0.000 3.920 0.000
	0.000 0.000 3.920
	Pt Pd
	3 1
	Direct
	0.500 0.500 0.000
	0.500 0.000 0.500
	0.000 0.500 0.500
	0.000 0.000 0.000

	1.000		
	5.549	0.000	0.000
	2.774	4.806	0.000
	2.775	1.602	4.532
	Pt Pd		
	7 1		
	Direct		
PtPd	0.000	0.000	0.000
	0.500	0.000	0.000
	0.000	0.500	0.000
	0.500	0.500	0.000
	0.000	0.000	0.500
	0.500	0.000	0.500
	0.000	0.500	0.500
	0.500	0.500	0.500

Table S2. INCAR file for geometric optimisation of bulks.

Global Parameters	
ISTART = 1	(Read existing wavefunction; if there)
ISPIN = 2	(Non-Spin polarised DFT)
# ICHARG = 11	(Non-self-consistent: GGA/LDA band structures)
LREAL = .FALSE.	(Projection operators: automatic)
ENCUT = 500	(Cut-off energy for plane wave basis set, in eV)
PREC = Normal	(Precision level)
LWAVE = .FALSE.	(Write WAVECAR or not)
LCHARG = .TRUE.	(Write CHGCAR or not)
ADDGRID = .TRUE.	(Increase grid; helps GGA convergence)
# LVTOT = .TRUE.	(Write total electrostatic potential into LOCPOT or not)
# LVHAR = .TRUE.	(Write ionic + Hartree electrostatic potential into LOCPOT or not)
# NELECT =	(No. of electrons: charged cells; be careful)
# LPLANE = .TRUE.	(Real space distribution; supercells)
# NPAR = 4	(Max is no. nodes; don't set for hybrids)
NCORE = 4	#NUMBER OF CORES PER ORBITAL
# Nwrite = 2	(Medium-level output)
# KPAR = 2	(Divides k-grid into separate groups)
# NGX = 500	(FFT grid mesh density for nice charge/potential plots)
# NGY = 500	(FFT grid mesh density for nice charge/potential plots)
# NGZ = 500	(FFT grid mesh density for nice charge/potential plots)
Electronic Relaxation	
ISMEAR = 1	(Gaussian smearing; metals:1)
SIGMA = 0.2	(Smearing value in eV; metals:0.2)
NELM = 90	(Max electronic SCF steps)
NELMIN = 6	(Min electronic SCF steps)
EDIFF = 1E-06	(SCF energy convergence; in eV)
GGA = PE	(PBEsol exchange correlation)
Ionic Relaxation	
NSW = 200	(Max ionic steps)
IBRION = 2	(Algorithm: 0-MD; 1-Quasi-New; 2-CG)
ISIF = 2	(Stress/relaxation: 2-Ions, 3-Shape/Ions/V, 4-Shape/Ions)
EDIFFG = -2E-02	(Ionic convergence; eV/AA)
# ISYM = 2	(Symmetry: 0=none; 2=GGA; 3=hybrids)
Dispersion interaction	
IVDW = 12	(Van der waals corrections - DFT-D3 method)

5.2. Input files for determination of electronic properties

Table S3. INCAR file for density of States and work function calculations.

```
general:
  ENCUT = 500
  SYSTEM = Pd3Pt
  ISPIN = 2
  ISMEAR = 1
  SIGMA = 0.2
  ALGO = Fast
  EDIFF = 1E-6
  LAECHG = .TRUE.

LDOS:
  LORBIT = 11
  LORBMOM = .TRUE.
  LMAXMIN = 4

workfunction:
  IDIPOL = 3
  LDIPOL = .TRUE.
  LVHAR = .TRUE.
  #LVTOT = .TRUE.

IVDW = 12
```

5.3. Input files for determination elastic constants

Table S4. INCAR file for determining elastic constants.

ISTART = 0	(Read existing wavefunction; if there)
ISPIN = 2	(Non-Spin polarised DFT)
LREAL = .FALSE.	(Projection operators: automatic)
ENCUT = 500	(Cut-off energy for plane wave basis set, in eV)
PREC = High	(Precision level)
LWAVE = .FALSE.	(Write WAVECAR or not)
LCHARG = .FALSE.	(Write CHGCAR or not)
ADDGRID = .TRUE.	(Increase grid; helps GGA convergence)
NCORE = 4	#NUMBER OF CORES PER ORBITAL
Electronic Relaxation	
ISMEAR = 1	(Gaussian smearing; metals:1)
SIGMA = 0.05	(Smearing value in eV; metals:0.2)
NELM = 40	(Max electronic SCF steps)
NELMIN = 4	(Min electronic SCF steps)
EDIFF = 1E-08	(SCF energy convergence; in eV)
GGA = PE	(PBEsol exchange-correlation)
Ionic Relaxation	
NSW = 100	(Max ionic steps)
NELMIN = 6	(Min electronic SCF steps)
IBRION = 2	(Algorithm: 0-MD; 1-Quasi-New; 2-CG)
ISIF = 2	(Stress/relaxation: 2-Ions, 3-Shape/Ions/V, 4-Shape/Ions)
EDIFFG = -1E-02	(Ionic convergence; eV/AA)
Dispersion interaction	
IVDW = 12	(Van der waals corrections - DFT-D3 method)

Table S5. Input file (VPKIT.in) for determining elastic constants.

2	! 1 for pre-processing; 2 for post-processing
3D	! 2D for two-dimensional, 3D for bulk
7	! number of strain case
-0.015 -0.010 -0.005 0.000 0.005 0.010 0.015 ! Strain range	

5.4. Input files for determination of phonon properties.

Table S6. CONTCAR file for Phonopy displacement 001 (PtPd₃).

```
generated by phonopy
1.00000
  7.8764  0.0000  0.0000
  0.0000  7.8764  0.0000
  0.0000  0.0000  7.8764
Pt Pd
8 24
Direct
0.0013 0.0000 0.0000
0.5000 0.0000 0.0000
0.0000 0.5000 0.0000
0.5000 0.5000 0.0000
0.0000 0.0000 0.5000
0.5000 0.0000 0.5000
0.0000 0.5000 0.5000
0.5000 0.5000 0.5000
0.2500 0.2500 0.0000
0.7500 0.2500 0.0000
0.2500 0.7500 0.0000
0.7500 0.7500 0.0000
0.2500 0.2500 0.5000
0.7500 0.2500 0.5000
0.2500 0.7500 0.5000
0.7500 0.7500 0.5000
0.2500 0.0000 0.2500
0.7500 0.0000 0.2500
0.2500 0.5000 0.2500
0.7500 0.5000 0.2500
0.2500 0.0000 0.7500
0.7500 0.0000 0.7500
0.2500 0.5000 0.7500
0.7500 0.5000 0.7500
0.0000 0.2500 0.2500
0.5000 0.2500 0.2500
0.0000 0.7500 0.2500
0.5000 0.7500 0.2500
0.0000 0.2500 0.7500
0.5000 0.2500 0.7500
0.0000 0.7500 0.7500
0.5000 0.7500 0.7500
```

Table S7. CONTCAR file for Phonopy displacement 002 (PtPd₃).

```
generated by phonopy
1.000
 7.8764 0.0000 0.0000
 0.0000 7.8764 0.0000
 0.0000 0.0000 7.8764
Pt Pd
8 24
Direct
0.0000 0.0000 0.0000
0.5000 0.0000 0.0000
0.0000 0.5000 0.0000
0.5000 0.5000 0.0000
0.0000 0.0000 0.5000
0.5000 0.0000 0.5000
0.0000 0.5000 0.5000
0.5000 0.5000 0.5000
0.2509 0.2500 0.0001
0.7500 0.2000 0.0000
0.2500 0.7500 0.0000
0.7500 0.7500 0.0000
0.2500 0.2500 0.5000
0.7500 0.2500 0.5000
0.2500 0.7500 0.5000
0.7500 0.7500 0.5000
0.2500 0.0000 0.2500
0.7500 0.0000 0.2500
0.2500 0.5000 0.2500
0.7500 0.5000 0.2500
0.2500 0.0000 0.7500
0.7500 0.0000 0.7500
0.2500 0.5000 0.7500
0.7500 0.5000 0.7500
0.0000 0.2500 0.2500
0.5000 0.2500 0.2500
0.0000 0.7500 0.2500
0.5000 0.7500 0.2500
0.0000 0.2500 0.7500
0.5000 0.2500 0.7500
0.0000 0.7500 0.7500
0.5000 0.7500 0.7500
```

Table S8. INCAR file for Phonopy calculation of sets of forces.

```
Global Parameters
PREC = Accurate
IBRION = -1
ENCUT = 500
EDIFF = 1.0e-08
ISMEAR = 0
SIGMA = 0.2
IALGO = 38
LREAL = .FALSE.
LWAVE = .FALSE.
LCHARG = .FALSE.
```

Table S9. mesh.conf file for Phonopy optimisation.

```
ATOM_NAME = Pt Pd3
DIM = 1 1 1
MP = 11 11 11
```

Table S10. pdos.conf file for Phonopy optimisation.

```
ATOM_NAME = Pt Pd3
DIM = 1 1 1
MP = 8 8 8
PDOS = 1, 2
```

Table S11. Band.conf file for Phonopy.

```
ATOM_NAME = Pt Pd
NPOINTS = 501
DIM = 1 1 1
PRIMITIVE_AXIS = AUTO
BAND = 0.000000 0.000000 0.000000 0.000000 0.500000 0.000000 0.500000 0.500000 0.000000 0.000000 0.000000
0.000000 0.500000 0.500000 0.500000 0.000000 0.500000 0.000000 0.500000 0.500000 0.500000 0.500000
0.000000
BAND_LABELS = $\Gamma$ X M $\Gamma$ Z R A Z X R M A
```

5.5. Molecular Dynamics – verification of dynamic stability

Table S12. INCAR file for MD simulations with changing temperature.

```
# where i = 100, 200, 300 , 400 , 500
SYSTEM = Pd

PREC = Accurate
ENCUT = 500.000
IBRION = 0
NSW = 100
ISIF = 2
NELMIN = 2
EDIFF = 1.0e-05
EDIFFG = -0.02
VOSKOWN = 1
ISYM = 0
SMASS = -1
POTIM = 1.0
NBLOCK = 2
TEBEG = i
TEEND = i
NWRITE = -1
NELM = 60
ALGO = Normal (blocked Davidson)
ISPIN = 1
INIWAV = 1
ISTART = 0
ICHARG = 2
LWAVE = .FALSE.
LCHARG = .FALSE.
ADDGRID = .FALSE.
ISMEAR = 1
SIGMA = 0.2
LREAL = .FALSE.
LSCALAPACK = .FALSE.
RWIGS = 1.28

# Default options for parallel
NPAR = 6
```

Table S13. KPOINT file for MD simulations.

```
Automatic mesh
0
Gamma
4 4 4
0. 0. 0.
```