Ab initio calculations of the elastic, electronic, optical, and vibrational properties of PdGa compound under pressure

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The structural, elastic, electronic, optical, and vibrational properties of cubic PdGa compound are investigated using the norm-conserving pseudopotentials within the local density approximation (LDA) in the frame of density functional theory. The calculated lattice constant has been compared with the experimental value and has been found to be in good agreement with experimental data. The obtained electronic band structures show that PdGa compound has no band gap. The second-order elastic constants have been calculated, and the other related quantities such as the Young's modulus, shear modulus, Poisson's ratio, anisotropy factor, sound velocities, and Debye temperature have also been estimated. Our calculated results of elastic constants show that this compound is mechanically stable. Furthermore, the real and imaginary parts of the dielectric function and the optical constants such as the electron energy-loss function, the optical dielectric constant and the effective number of electrons per unit cell are calculated and presented in the study. The phonon dispersion curves are also derived using the direct method.

Keywords: PdGa, vibrational properties, optical properties, elastic constants

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1. Introduction

PdGa as structurally well-ordered intermetallic compounds[1−7] have recently been explored as highly selective heterogeneous hydrogenation catalysts in the semi-hydrogenation of acetylene.[8,9] To understand the excellent heterogeneous catalytic properties of the intermetallic compound PdGa in detail, large single crystals are necessary to conduct surface investigations.[10] PdGa crystallizes in the FeSi type of structure.[11,12] The FeSi type of structure may be considered as strongly distorted NaCl type with associated increase in coordination number from 6 to 7 for both atom sites.[13] The coordination shell of Pd or Ga, respectively, consist exlusively of atoms of the other kind and may be described as distorted monocapped trigonal prism.[10] The intermetallic compound PdGa posses metallic conductivity, a well-defined crystal structure as well as partly covalent bonding between the atoms.[7] According to Armbrüster et al.[10] the crystal structures of PdGa is simple cubic with space group $P2_13$ (No:198). PdGa has 8 atoms (four molecules) per unit cell. Pd atoms are positioned at Whckoff 4a (0.39240, 0.39240, 0.39240) sites, while Ga atoms are positioned at Whckoff 4a (0.09295, 0.09295, 0.09295) sites.

Here, we present the results of our *ab initio* calculations on the structural, mechanical electronic, optical, and vibrational properties of PdGa. To our knowledge, these properties have not been considered so far for PdGa. Consequently, the main purpose of this work is to provide some additional information to the existing data on the physical properties of PdGa by using the *ab initio* total energy calculations. To this end, we have estimated the bulk modulus, elastic constants, Young's modulus, shear modulus, Poisson's ratio, anisotropy factor, sound velocities, Debye temperature, and phonon frequencies of PdGa compound for the first time. The calculation method is given in Section 2. The results are discussed in Section 3. Finally, the conclusions are presented in Section 4.

2. Calculation methods

The calculations were performed using the density functional formalism and local density ap-

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proximation (LDA)[14] through the Ceperley and Alder functional[15] as parameterized by Perdew and Zunger[16] for the exchange-correlation energy in the SIESTA code.[17,18] This code calculates the total energies and atomic forces using a linear combination of atomic orbitals as the basis set. The basis set is based on the finite range pseudoatomic orbitals (PAOs) of the Sankey–Niklewsky type,[19] generalized to include multiple-zeta decays.

The interactions between electrons and core ions are simulated with separable Troullier–Martins[20] norm-conserving pseudopotentials. We have generated atomic pseudopotentials separately for atoms Pd and Ga by using the $5s^1 4d^9$ and $4s^2 4p^1$ configurations, respectively. The cut-off radii for present atomic pseudopotentials are taken to be 2.58 a.u. for s channels, 2.71 a.u. for p channels, and 2.45 a.u. for the d and f channels of Pd; 2.18 a.u. for s channels, 2.47 a.u. for p channels, and 2.59 a.u. for the d and f channels of Ga.

The SIESTA code calculates the self-consistent potential on a grid in real space. The fineness of this grid is determined in terms of a cut-off energy $E_{\rm c}$ in analogy to the cut-off energy when the basis set involves plane waves. Here by using a double-zeta plus polarization (DZP) orbital basis and the cut-off energies between 100 and 450 Ry with various basis sets, we found an optimal value of around 375 Ry for PdGa. For the final computations, 75 k-points for PdGa were enough to obtain the converged total energy ΔE to about 1 meV per atom.

It is known that the dielectric function is mainly connected with the electronic response. The dielectric function was calculated in the momentum representation, which requires matrix elements of the momentum $\boldsymbol{p}$ between occupied and unoccupied eigenstates. The imaginary part of the dielectric function, $\varepsilon_2(\omega)$, is given by

$$\begin{aligned}\varepsilon_2(\omega) = {} & \frac{Ve^2}{2\pi\hbar m^2\omega^2}\int \mathrm{d}^3k \sum_{n,n'} |\langle \boldsymbol{k}n\,|\boldsymbol{p}|\,\boldsymbol{k}n'\rangle|^2 \\ & \times x f(\boldsymbol{k}n')\left[1-f(\boldsymbol{k}n')\right]\delta \\ & \times \left(E_{\boldsymbol{k}n}-E_{\boldsymbol{k}nn'}-\hbar\omega\right), \end{aligned} \tag{1}$$

where e is the electron charge, m is the electron mass, V is the volume, $|\boldsymbol{k}n\rangle$ is a crystal wave function, $\boldsymbol{p}$ is the momentum operator, $f(\boldsymbol{k}n)$ is the Fermi function, $E_{\boldsymbol{k}n}$ is the energy of the electron in the nth state, and $\hbar\omega$ is the energy of the incident photon with h being Planck constant, and w the photon frequency. The summation over the Brillouin zone (BZ) is the calculation using a linear interpolation on a mesh of uniformly distributed points. Matrix elements, eigenvalues, and eigenvectors are calculated in the irreducible part of the BZ.

As is known, the Kohn–Sham equations determine the ground-state properties. Thus, when the optical response calculations are made, the self-energy effect must be included. Otherwise the unoccupied conduction bands have no physical significance and a band gap problem appears: the absorption starts at a quite low energy.

The real part of the dielectric function, $\varepsilon_1(\omega)$, is evaluated from the imaginary part $\varepsilon_2(\omega)$ by the Kramer–Kronig transformation. All other optical constants such as electron energy-loss function, effective number of valance, and effective optical dielectric constant can be derived from the real and imaginary parts of the dielectric function using the expressions in Ref. [21].

3. Results and discussion

3.1. Structural properties

The equilibrium lattice constant, the bulk modulus, and its pressure derivative have been computed minimizing the crystal's total energy calculated for the different values of lattice constant by means of Murnaghan's equation of states (EOS),[22] and the results are shown in Table 1 along with the experimental value. The lattice constant for PdGa compound is found to be $a_0 = 4.88$ Å, and it is in a good agreement with the experimental value.[10] In all our calculations, we have used the computed lattice constant. In the present case, the calculated bulk modulus for

Table 1. The calculated equilibrium lattice constant (a_o), bulk modulus (B), and the pressure derivative of bulk modulus (B') together with the experimental value for PdGa.

Material	a_0/Å		B/GPa		B'	
	This work	Exp.[a)]	This work	Exp.[a)]	This work	Exp.[a)]
PdGa	4.88	4.90	179.02	–	4.14	–

[a)] Ref. [10].

PdGa is 179.02 GPa. Unfortunately, there are no theoretical and experimental results for comparing with calculated bulk modulus.

3.2. Elastic properties

The elastic constant of solids provides a link between the mechanical and dynamical behavior of crystals, and give important information concerning the nature of the forces operating in solids. In particular, they provide information on the stability and stiffness of materials, and their ab initio calculation requires precise methods. Since the forces and the elastic constants are functions of the first-order and second-order derivatives of the potentials, their calculation will provide a further check on the accuracy of the calculation of forces in solids. They also provide valuable data for developing inter atomic potentials.

Here, to compute the elastic constants (C_{ij}), we have used the volume-conserving technique.[23] The elastic constants are calculated to be $C_{11} = 267.27$ GPa, $C_{12} = 134.90$ GPa, and $C_{44} = 51.98$ GPa for PdGa. Unfortunately, there are no theoretical and experimental results for comparing with the present results. Then, our results can serve as a prediction for future investigations.

The traditional mechanical stability conditions in cubic crystals on the elastic constant are known as $C_{11} - C_{12} > 0$, $C_{11} > 0$, $C_{44} > 0$, and $C_{11} + 2C_{12} > 0$. Our calculated elastic constants not only obey these stability conditions for cubic PdGa compound, but also obey the other cubic stability condition, $C_{12} < B < C_{11}$.

The other principal goal of the present work is to report the pressure dependency of the second-order elastic constant (SOEC) and bulk modulus for PdGa.

As can be seen in Fig. 1, elastic constants C_{11}, C_{12}, and bulk modulus (B) increase monotonically with pressure, and the slope for C_{44} is relatively low. The elastic constant C_{11} represents elasticity in length. A longitudinal strain produces a change in C_{11}. The elastic constants C_{12} and C_{44} are related to the elasticity in shape, which is a shear constant. A transverse strain causes a change in shape without a change in volume. Therefore, C_{12} and C_{44} are less sensitive to pressure as compared with C_{11}. According to Johnson[24] and Pettifor,[25] the angular character of atomic bonding in metals and compounds could be described by the Cauchy pressure (C_{12}–C_{44}). If the bonding in character is metallic, the Cauchy pressure is typically positive. Furthermore, for directional bonding with angular character, the Cauchy pressure is negative. The calculated C_{12}–C_{44} values are positive at all pressures. We can say that PdGa has metallic bonding character.

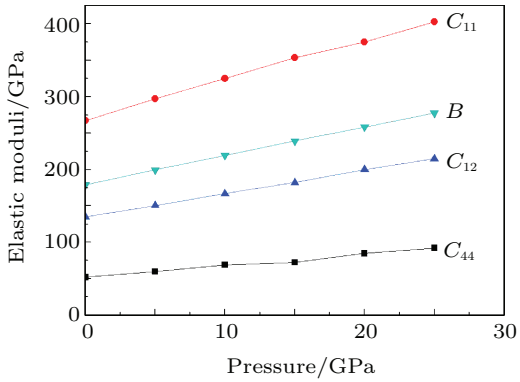


Fig. 1. (colour online) Pressure dependence of $C_{ij}$and bulk modulus for PdGa.

The Zener anisotropy factor A, Poisson's ratio v, and Young's modulus Y, which are the most interesting elastic properties for the technological applications, are also calculated in terms of the computed data using the following relations:[26]

$$A = \frac{2C_{44}}{C_{11} - C_{12}}, \tag{2}$$

$$v = \frac{1}{2}\left[\frac{(B - (2/3)\,G)}{B + (1/3)\,G}\right], \tag{3}$$

$$Y = \frac{9GB}{G + 3B}, \tag{4}$$

where $G = (G_{\rm V} + G_{\rm R})/2$ is the isotropic shear modulus, $G_{\rm V}$ is Voigt's shear modulus corresponding to the upper bound of G values, and $G_{\rm R}$ is Reuss's shear modulus corresponding to the lower bound of G values. They can be written as $G_{\rm V} = (C_{11} - C_{12} + 3C_{44})/5$, and $G_{\rm R} = 5(C_{11} - C_{12})C_{44}/[4C_{44} + 3(C_{11} - C_{12})]$.

The Zener anisotropy factor (A), Poisson's ratio (v), Young's modulus (Y), and isotropic shear modulus for PdGa are calculated to be 0.79, 0.34, 155.23 GPa, and 57.26 GPa, respectively. The Zener anisotropy factor is an indicator of the degree of anisotropy in the solid structure. For a completely isotropic material, the factor A takes the value of 1. When the value is smaller or greater than unity, it is a measure of the degree of elastic anisotropy. The calculated Zener anisotropy factor (0.79), therefore, demonstrates that this material has a very small elastic anisotropy. The value of the Poisson's ratio is indicative of the degree of directionality of the covalent bonds. The value of the Poisson's ratio is almost 0.1 for covalent materials, whereas for ionic materials, a

typical value is 0.25.[27] The calculated Poisson's ratio is 0.34, indicating that ionic contributions in inter atomic bonding are dominant for this compound.

According to criterion,[28,29] a material is brittle (ductility) if the B/G ratio is less (higher) than 1.75. The calculated values of the B/G for PdGa are higher than 1.75. Hence, this structure behaves in a ductile manner. Moreover, for covalent and ionic materials, the typical relations between bulk and shear moduli are $G \cong 1.1$ B and $G \cong 0.8$ B, respectively.[27] Since the present value of G/B is lower than 0.8, this result strongly supports the ionic contribution to inter atomic bonding.

The variations of Young's and shear moduli under pressure are depicted in Fig. 2(a), and both curves show almost similar trends under the pressures considered. In Fig. 2(b), the Anisotropy factor (A) increases with pressure in the studied pressure range, but the decreasing rate of the Poisson's ratio is quite small and almost remains unchanged for the same pressure interval. According to Frantsevich rule,[30] the critical value of a material is 0.33 for brittle materials, the Poisson's ratio is lees than 0.33, otherwise the material behaves in a ductile manner.[31] It is identified from Fig. 2(b) that at increasing pressure, the Poisson's ratio shows the ductile nature.

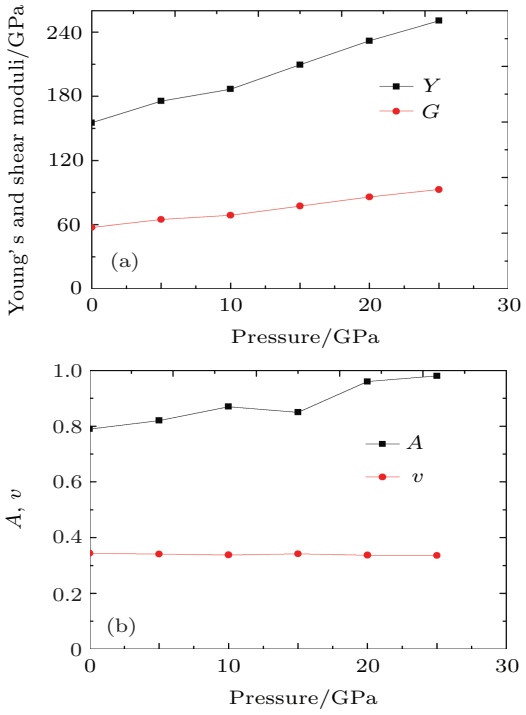


Fig. 2. (colour online) Pressure dependences of (a) Young's and shear moduli, (b) Zener anisotropy factor (A), and Poisson's ratio (v), for PdGa.

The Debye temperature is known as an important fundamental parameter closely related to many physical properties such as specific heat and melting temperature. At low temperatures the vibrational excitations arise solely from acoustic vibrations. Hence, at low temperatures the Debye temperature calculated from elastic constants is the same as that determined from specific heat measurements. We have calculated the Debye temperature, $\theta_{\rm D}$, from the elastic constant data using the average sound velocity, $v_{\rm m}$, by the following common relation given in Ref. [32]:

$$\theta_{\rm D} = \frac{h}{k}\left[\frac{3n}{4\pi}\left(\frac{N_{\rm A}\rho}{M}\right)\right]^{1/3} v_{\rm m}, \tag{5}$$

where k is Boltzmann's constant, $N_{\rm A}$ is Avogadro's number, n is the number of atoms per formula unit, M is the molecular mass per formula unit, $\rho(= M/V)$ is the density, and $v_{\rm m}$ is given by[33]

$$v_{\rm m} = \left[\frac{1}{3}\left(\frac{2}{v_{\rm t}^3} + \frac{1}{v_{\rm l}^3}\right)\right]^{-1/3}, \tag{6}$$

where $v_{\rm l}$ and $v_{\rm t}$ are the longitudinal and transverse elastic wave velocities, respectively, which are obtained from Navier's equations[34]

$$v_{\rm l} = \sqrt{\frac{3B + 4G}{3\rho}}, \tag{7}$$

$$v_{\rm t} = \sqrt{\frac{G}{\rho}}\,. \tag{8}$$

The calculated Debye temperature and sound velocities are given in Table 2. The pressure variation of Debye temperature up to 25 GPa is depicted in Fig. 3(a). We have limited ourselves up to 25 GPa due to the considerable time consumed in the calculations of elastic data at various pressures. It increases (not linearly) with increasing pressures. The calculated value of Debye temperature for PdGa compound at zero pressure is 323.57 K. Increase in Debye temperature indicates decrease in the effective ionic distance among Pd and Ga atoms.[35] To explain the variation of θ_D with the pressure, we attempt to analyze our results in the framework of dynamics of lattice with pressure. The pressure-induced change of the force constants leads to the increase in θ_D. Moreover, the variation of θ_D with increasing pressure suggests that increasing Debye temperature drives effectively the system toward the hardening of lattice. Unfortunately, there are no theoretical and experimental results to be compared with the calculated $v_{\rm l}$, $v_{\rm t}$, $v_{\rm m}$, and θ_D values.

Table 2. Calculated density, longitudinal, transverse, and average elastic wave velocities, and Debye and melting temperatures for PdGa.

ρ/g · cm^{-3}	$v_{\rm l}$/m · s^{-1}	$v_{\rm t}$/m · s^{-1}	$v_{\rm m}$/m · s^{-1}	$\theta_{\rm D}$/K	$T_{\rm m}$/K
10.81	4860.37	2301.51	2589.53	323.57	2135.57

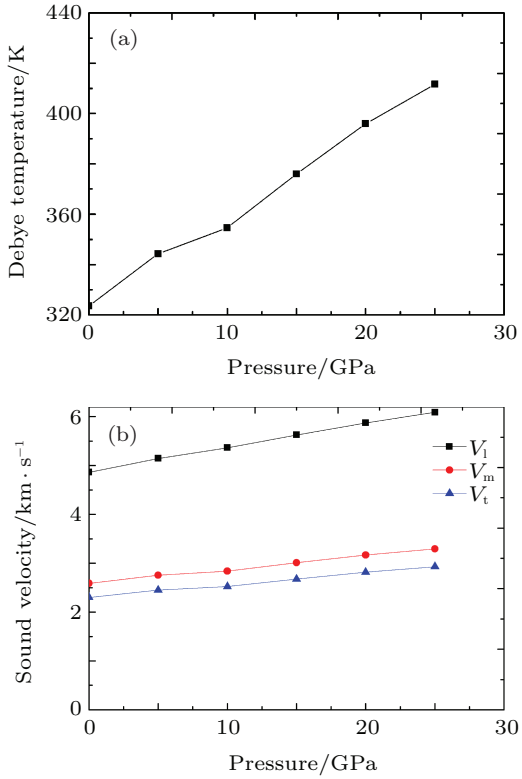


Fig. 3. (colour online) Pressure dependence of (a) Debye temperature and (b) sound velocities for PdGa.

The calculated values of the longitudinal, transverse, and average sound velocities in the present formalism are given in Table 2 along with the Debye temperature and the melting temperature. Figure 3(b) shows the calculated pressure-dependent behaviour of the sound velocity up to 25 GPa for the same compound. The average and transverse wave velocities exhibit a similar trend: slowly increase with pressure, and the increasing rate of the longitudinal wave velocity is, relatively, slightly higher.

The empirical relation,[36] $T_m = 553 + (591/10^{11})C_{11} \pm 300$ K, is used to estimate the melting temperature, and found to be 2135 ± 300 K. This value is higher than that obtained for Pd (1825 K), and much higher (about seven times) than that of Ga (302 K). We hope that the present result is a reliable estimation for PdGa as it only contains C_{11}.

3.3. Electronic properties

For a better understanding of the electronic and optical properties of PdGa compound, the investigation of the electronic band structure would be useful. We first describe our calculated electronic structure. The energy-band structure calculated using LDA for cubic PdGa is shown in Fig. 4.

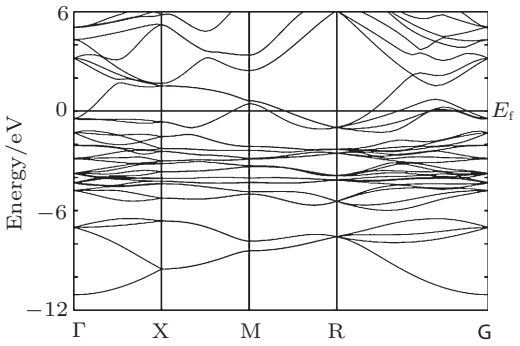


Fig. 4. The calculated band structures of PdGa. The position of the Fermi level is at 0 eV.

The band structure calculations have been performed in the high-symmetry directions of the first BZ. The band structure of PdGa has been calculated and plotted on the surface of the BZ. It can be seen from Fig. 4 that no band gap exists in the band structure, exhibiting a metallic feature. The k points, marked with letters in Fig. 4, denote the corners of the irreducible BZ. The Fermi level is set to be zero.

To understand the mechanical properties of this material on a fundamental level, the partial densities of states (PDOSs) are calculated at zero pressure using LDA. The results are shown in Fig. 5 along with the Fermi energy level. In Fig. 4, the main components of the PDOS at the bottom of the conduction band (CB) are the mixings of the Pd and Ga valance orbitals. The states in the valance band (VB) between –11 and –7 eV are mainly composed of Ga (4s) and Pd (5s) states. The other valance bands are essentially dominated by Pd (4d) states. The 4s and 4p states of Ga atoms also contribute to the valance bands, but the values of density of these states are quite small compared with Pd 4d. In view of the quantitative analysis of the overlap extent between the Pd (4d) and Ga (4p) states, as shown in Fig. 5, we find that the overlap extent between the Pd (4d) and Ga (4p) are small. For this reason, we can conclude that PdGa has a highly ionic character and small shear modulus.

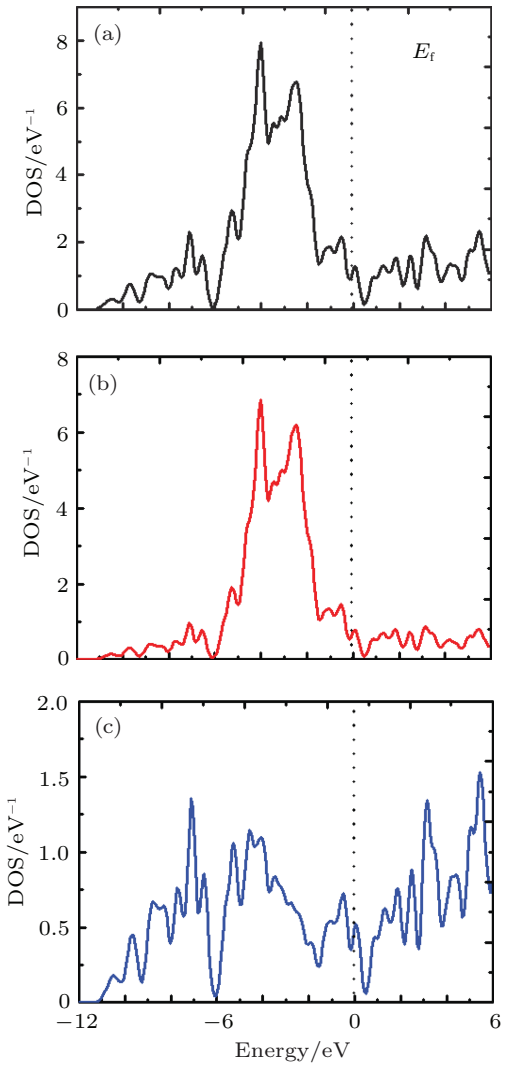


Fig. 5. (colour online) (a) Total density of states for PdGa. Projected density of states for (b) Pd and (c) Ga. The position of the Fermi level is at 0 eV.

3.4. Optical properties

The linear optical properties of PdGa are investigated. The calculated optical functions are shown in Fig. 6. The calculations neglect all lattice vibrational effects and only pertain to electronic transitions. In order to calculate the optical response, using the calculated band structure, we have chosen a photon-energy range of 0–14 eV and have seen that a photon-energy range from 0 to 2 eV is sufficient for most optical functions. Thus, we have derived the values of real and imaginary parts of the dielectric function as functions of the photon energy.

We first calculated the real and imaginary parts of the frequency-dependent linear dielectric function, as shown in Fig. 6. The peaks of ε_2 correspond to the optical transitions from the valence band to the conduction band. The maximum peak value of ε_2 for PdGa are around 0 eV. In general, there are various contributions to the dielectric function, but figure 6 only shows the contribution of the electronic polarizability to the dielectric function. In the range between 0 and 0.4 eV, the ε_1 decreases with increasing photon energy, which is characteristic of an anomalous dispersion. In this energy range, the transitions between occupied and unoccupied states mainly occur between Pd 4d states which can be seen in the DOS (PDOS) displayed in Fig. 5. The ε_1 is equal to zero at about 0.23 eV and 14.09 eV. The interband transitions at these points, which consist mostly of plasmon excitations, and the scattering probability of volume losses are directly connected with the energy-loss function[36]

$$L(\omega) = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2}. \tag{9}$$

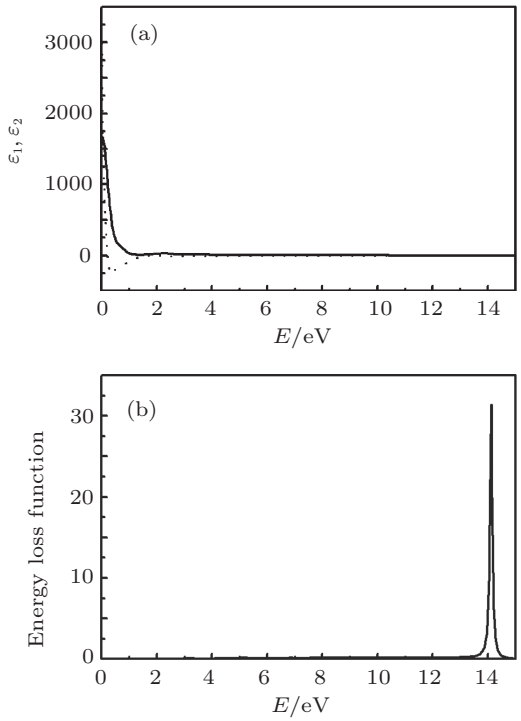


Fig. 6. Energy spectra of (a) dielectric function $\varepsilon = \varepsilon_1 - \mathrm{i}\varepsilon_2$ and (b) energy-loss function (L) for PdGa.

The calculated energy-loss functions, $L(\omega)$, are also presented in Fig. 6. The energy-loss functions describe the energy loss of the fast electrons transversing the material. The sharp maxima in the energy-loss function are associated with the existence of plasma oscillations.[38] The curves of L in Fig. 6 have a maximum near 14.09 eV for PdGa.

The known sum rules[39] can be used to determine some quantitative parameters, particularly the effective number of the valence electrons per unit cell N_{eff}, as well as the effective optical dielectric constant $\varepsilon_{\mathrm{eff}}$,

which make a contribution to the optical constants of a crystal at the energy E_0. We recall that

$$N_{\rm eff}(E) = \frac{2m\varepsilon_0}{\pi\hbar^2 e^2 N_{\rm a}} \int_0^{\infty} \varepsilon_2(E) E \,{\rm d}E, \quad (10)$$

$$\varepsilon_0(E) - 1 = \frac{2}{\pi} \int_0^{\infty} \varepsilon_2(E) E^{-1} \,{\rm d}E, \quad (11)$$

where $N_{\rm a}$ is the density of atoms in a crystal, and $N_{\rm eff}(E_0)$ s the effective number of electrons contributing to optical transitions below an energy of E_0. The physical meaning of $\varepsilon_{\rm eff}$ is quite clear: $\varepsilon_{\rm eff}$ is the effective optical dielectric constant governed by the interband transitions in the energy range from zero to E_0, i.e., by the polarization of the electron shells. The calculated effective number of valence electrons $N_{\rm eff}$ and the effective dielectric constant $\varepsilon_{\rm eff}$ are given in Fig. 7. The effective number of valence electron per unit cell, $N_{\rm eff}$, contributing in the interband transitions, reaches the saturation value at about 12 eV. This means that deep-lying valence orbitals participate in the interband transitions as well (see Fig. 4).

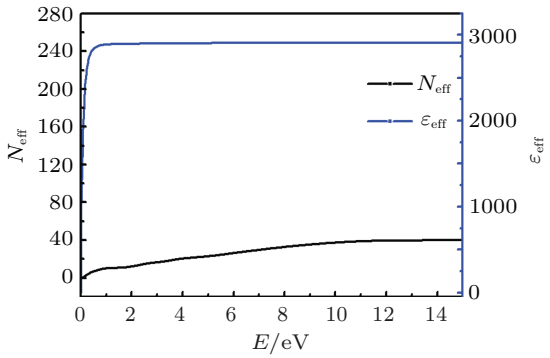


Fig. 7. (colour online) Energy spectra of $N_{\rm eff}$ and $\varepsilon_{\rm eff}$ for PdGa.

The effective optical dielectric constant, $\varepsilon_{\rm eff}$, shown in Fig. 7, reaches a saturation value at about 1 eV. This means that the greatest contribution to $\varepsilon_{\rm eff}$ arises from interband transitions between 0 and 1 eV.

3.5. Lattice dynamical properties

The phonon dispersion curves and phonon density of state have been calculated with the direct method[40] as implemented in the phonon software.[41] The force constants and dynamical matrices have been obtained from the Hellmann–Feynman forces calculated with small individual displacements of nonequivalent atoms. The displacement amplitudes are taken as 0.03 Å. To increase the precision and minimize the anharmonic effects, the positive and negative atomic displacements along x, y, and z axes are taken into account.

The obtained phonon dispersion curves and the corresponding one-phonon DOS for this compound along the high-symmetry directions are illustrated in Fig. 8. Unfortunately, there are no other theoretical or experimental results to be compared with the present work. The unit cell of PdGa contains 8 atoms, which give rise to a total of 24 phonon branches, which contains 3 acoustic modes and 21 optical modes. The calculated phonon dispersion curves have no soft mode at any vectors, which confirms the dynamical stability of PdGa compound.

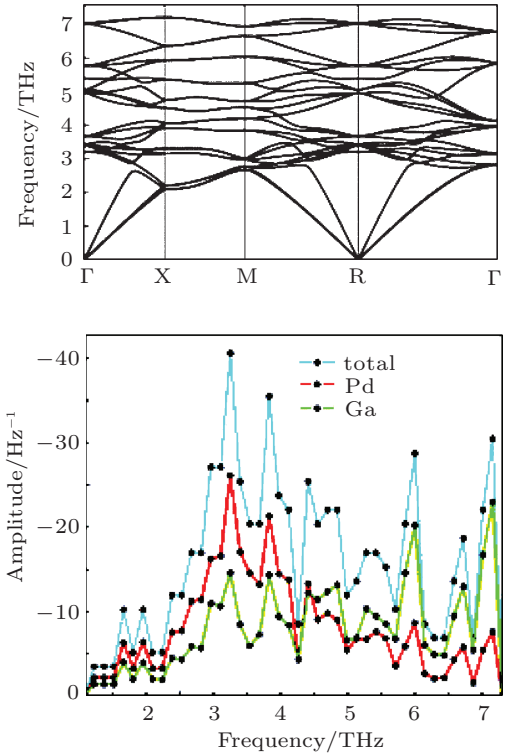


Fig. 8. (colour online) (a) Calculated phonon dispersion curves. (b) Total and partial densities of states.

In Fig. 8(b), the corresponding partial density of phonon states are plotted for this compound. It is observed that the main contribution to lower phonons comes from the Pd atom sublattice, and the high-frequency phonons stem from the Ga atoms. This is expected because the Ga atom is lighter than Pd atom.

4. Conclusion

In the present work, we have made a detailed investigation of the structural, electronic, mechanical,

optical, and vibrational properties of the PdGa compound using the density functional methods. We have revealed that the cubic PdGa compound is in the ground-state configuration and the band structures of this compound are metallic in nature. The elastic constants obtained using volume-conserving technique shows that this compound is mechanically stable. The related mechanical and dynamical properties like shear modulus, Young's modulus, Poisson's ratio, Debye temperature, shear anisotropic factors, and phonon properties are calculated and discussed. We have examined photon-energy-dependent dielectric functions, some optical properties such as the energy-loss function, the effective number of valance electrons, and the effective optical dielectric constant, and mechanical properties. The calculated phonon dispersion curves have no soft mode at any vectors, which confirms the stability of PdGa. Since there are no experimental elastic data available for PdGa compound, we think that the *ab initio* theoretical estimation is the only reasonable tool for obtaining such important information.

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