First-principles study of the structural, elastic, electronic, optical, and vibrational properties of intermetallic Pd_2Ga

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The structural, elastic, electronic, optical, and vibrational properties of the orthorhombic Pd_2Ga compound are investigated using the norm-conserving pseudopotentials within the local density approximation in the frame of density functional theory. The calculated lattice parameters have been compared with the experimental values and found to be in good agreement with these results. The second-order elastic constants and the other relevant quantities, such as the Young's modulus, shear modulus, Poisson's ratio, anisotropy factor, sound velocity, and Debye temperature, have been calculated. It is shown that this compound is mechanically stable after analysing the calculated elastic constants. Furthermore, the real and imaginary parts of the dielectric function and the optical constants, such as the optical dielectric constant and the effective number of electrons per unit cell, are calculated and presented. The phonon dispersion curves are derived using the direct method. The present results demonstrate that this compound is dynamically stable.

Keywords: Pd_2Ga, vibrational properties, optical properties, elastic constants

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1. Introduction

Selective hydrogenation of acetylene is an important industrial process to remove the traces of acetylene in the ethylene feed for the production of polyethylene. Because acetylene poisons the catalyst for the polymerization of ethylene to polyethylene, the acetylene component in the ethylene feed has to be reduced to a low percent per million range. Moreover, economic efficiency requires high selectivity of the acetylene hydrogenation in the presence of an excess of ethylene to prevent the hydrogenation of ethylene to ethane.[1−4]

Among the Pd-X materials investigated for use as hydrogenation catalysts, bulk Pd–Ga intermetallic compounds (IMCs) have shown extraordinarily high selectivity and stability in the semi-hydrogenation of acetylene. The IMCs are single-phase materials which consist of two or more metallic elements. In contrast to alloys, they have an ordered crystal structure that us different from those of the constituting metals themselves. Thus, their chemical properties may also differ substantially, and they should be considered as a class of materials in their own right, requiring an independent physicochemical characterization. The well-defined intermetallic compounds Pd_2Ga, PdGa and Pd_3Ga_7 have been shown to be excellent catalysts for the semi-hydrogenation of acetylene.[5−7] In the intermetallic compounds Pd_2Ga, PdGa and Pd_3Ga_7, the Pd atoms are only surrounded by the Ga atoms in the first coordination shell and thus these compounds may be promising catalysts with improved selectivity and long-term stability in acetylene hydrogenation.[8]

Recently, Pd_2Ga has been synthesized by Kovnir *et al.*[9] and the crystal structure of Pd_2Ga is found to be orthorhombic. The orthorhombic unit cell of Pd_2Ga belongs to the space group $Pnma$–D_{2h}^{16}. The crystal has four Pd_2Ga molecules in a unit cell. Two Pd atoms are positioned at Wyckoff 4c (0.16511, 0.25, 0.06662) and Wyckoff 4c (0.04293, 0.25, 0.71063) sites, respectively, while Ga atoms are positioned at Wyckoff 4c (0.2016, 0.25, 0.39316) sites.

In this paper, we present the results of *ab initio* calculations of the structural, electronic, optical, mechanic, and vibrational properties of Pd_2Ga. To our knowledge, these properties have not been considered

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for Pd_2Ga so far. Consequently, the main purpose of this work is to provide some additional information to the existing data regarding the physical properties of Pd_2Ga by using *ab initio* total energy calculations. The calculation method is introduced in Section 2. The results are discussed in Section 3. Finally, the conclusion is presented in Section 4.

2. Calculation methods

The calculations have been performed using the density functional formalism and the local density approximation (LDA)[10] through the Ceperley–Alder functional[11] as parameterized by Perdew and Zunger[12] for the exchange-correlation energy in the SIESTA code.[13,14] This code can be applied to calculate the total energy (ΔE) and atomic force using a linear combination of atomic orbitals as the basis set. The basis set is based on the finite range pseudo-atomic orbitals of the Sankey–Niklewsky type,[15] which is generalized to include multiple-zeta decays.

The interactions between electrons and core ions are simulated with separable Troullier–Martins[16] norm-conserving pseudopotentials. The atomic pseudopotentials for Pd and Ga atoms are generated by using the $5s^1 4d^9$ and $4s^2 4p^1$ configurations, respectively. The cut-off radii for the present pseudopotentials of Pd atoms are chosen to be 2.58 a.u. for s channels, 2.71 a.u. for p channels, and 2.45 a.u. for d and f channels. In the case of Ga atoms, the cut-off radii are chosen to be 2.18 a.u. for s channels, 2.47 a.u. for p channels, and 2.59 a.u. for d and f channels.

The SIESTA code is applied to calculate the self-consistent potential on a grid in real space. The fineness of this grid is determined by a cut-off energy (E_c) in analogy to the cut-off energy when the basis set involves plane waves. By using a double-zeta plus polarization (DZP) basis set and various other basis sets where the cut-off energy is from 100 to 450 Ry, we find an optimal value of around 325 Ry for Pd_2Ga. For the final computations, 30 $\boldsymbol{k}$ points are enough for Pd_2Ga to obtain the converged total energy ΔE of about 1 meV per atom.

3. Results and discussion

3.1. Structural properties

All physical properties are related to the total energy. For instance, the equilibrium lattice constant of a crystal is the lattice constant that minimizes the total energy. If the total energy is calculated, any physical properties relevant to the total energy can be determined.

Firstly, the equilibrium lattice parameters (a, b, and c), the bulk modulus (B), and the pressure derivative of B (B') have been computed via minimizing the crystal's total energy calculated for different values of lattice constant by means of Murnaghan's equation of states.[17] The calculated results along with the experimental values are shown in Table 1. The lattice parameters a, b, and c for Pd_2Ga are respectively calculated to be 5.4816, 4.0545, and 7.808 Å and they are in good agreement with the experimental values.[9] In all our calculations, we have used these values of lattice parameters. In the present case, the calculated bulk modulus for Pd_2Ga is 194.01 GPa. Unfortunately, there are no theoretical and experimental results to compare with the calculated bulk modulus.

Table 1. The calculated equilibrium lattice parameters, bulk modulus, and pressure derivative of bulk modulus together with the experimental values for Pd_2Ga.

	a/Å	b/Å	c/Å	B/GPa	B'
Present (LDA)	5.4816	4.0545	7.808	194.01	5.06
Experimental	5.4829	4.0560	7.7863	–	–

3.2. Elastic properties

The elastic constants of solids provide not only a link between the mechanical and dynamical behaviour of crystals, but also important information concerning the nature of the force operating in materials. In particular, they provide information on the stability and stiffness of materials, and their *ab initio* calculation requires precise methods. Since the force 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 force in materials. They also provide valuable data for developing interatomic potentials. Here, to calculate the elastic constants, we have used the volume-conserving technique.[18] Unfortunately, there are no theoretical results available to compare with the present work. Thus, our results can serve as a reference for future investigations.

Nine independent strains are necessary to calculate the elastic constants of the orthorhombic Pd_2Gacompound. The mechanical stability requires the following restrictions on the elastic constants of

an orthorhombic crystal:[18−20]

$$(C_{11}+C_{22}-2C_{12})>0,\quad (C_{11}+C_{33}-2C_{13})>0,$$
$$(C_{22}+C_{33}-2C_{23})>0,\quad C_{11}>0,\ C_{22}>0,$$
$$C_{33}>0,\ C_{44}>0,\quad C_{55}>0,\ C_{66}>0,$$
$$(C_{11}+C_{22}+C_{33}+2C_{12}+2C_{13}+2C_{23})>0. \quad (1)$$

The calculated elastic constants (in GPa) that obey the above stability conditions for Pd_2Ga are as follows: $C_{11}=276.2$, $C_{22}=249.92$, $C_{33}=268.76$, $C_{12}=137.65$, $C_{13}=139.06$, $C_{23}=148.49$, $C_{44}=65.51$, $C_{55}=40.35$, and $C_{66}=74.47$. The elastic constants C_{11}, C_{22}, and C_{33} determine the resistance-to-linear compression in the a-, b-, and c-directions, respectively. The calculated C_{22} for Pd_2Ga is lower than C_{11} and C_{33}. Thus, the b-axis of Pd_2Ga is more compressible than the a and c-axis.

It is known that the elastic constant C_{44} is the most important parameter indirectly governing the indentation hardness of a material. A large C_{44} means a strong resistance to the monoclinic shear distortion in the (100) plane, and the C_{66} is related to the resistance to the shear in the $\langle 110\rangle$ direction. The calculated C_{44} and C_{66} for Pd_2Ga are 65.51 and 74.47 GPa, respectively.

A problem arises when single crystal samples are not available, since it is then not possible to measure the individual elastic constants. Instead, the polycrystalline bulk modulus and the shear modulus (G) may be determined. There are two approximation methods to calculate the polycrystalline modulus, namely, the Voigt method[21] and the Reuss method.[22] For specific cases of orthorhombic lattices, the Reuss shear modulus ($G_{\rm R}$) and the Voigt shear modulus ($G_{\rm V}$) satisfy

$$\frac{1}{G_{\rm R}}=\frac{4}{15}(s_{11}+s_{22}+s_{33})-\frac{4}{15}(s_{12}+s_{13}+s_{23})+\frac{3}{15}(s_{44}+s_{55}+s_{66}), \quad (2)$$

and

$$G_{\rm V}=\frac{1}{15}(C_{11}+C_{22}+C_{33}-C_{12}-C_{13}-C_{23})+\frac{1}{5}(C_{44}+C_{55}+C_{66}), \quad (3)$$

and the Reuss bulk modulus ($B_{\rm R}$) and the Voight bulk modulus ($B_{\rm V}$) are defined as

$$B_{\rm R}=\frac{1}{(s_{11}+s_{22}+s_{33})+2(s_{12}+s_{13}+s_{23})}, \quad (4)$$

and

$$B_{\rm V}=\frac{1}{9}(C_{11}+C_{22}+C_{33})+\frac{2}{9}(C_{12}+C_{13}+C_{23}). \quad (5)$$

In Eqs. (2) and (4), s_{ij} is the elastic compliance constant. Using energy considerations Hill[23] proved that the Voigt and Reuss equations represent the upper and lower limits of the true polycrystalline constants, and recommended that a practical estimate of the bulk and shear moduli were the arithmetic means of the limits. Hence, the elastic moduli of a polycrystalline material can be approximated by Hill's average and the shear modulus is

$$G=\frac{1}{2}(G_{\rm R}+G_{\rm V}), \quad (6)$$

and the bulk modulus is given by

$$B=\frac{1}{2}(B_{\rm R}+B_{\rm V}). \quad (7)$$

The Young's modulus (E) and Poisson's ratio (v) for an isotropic material are given by $E=9BG/(3B+G)$ and $v=(3B-2G)/2(3B+G)$, respectively.[24,25] Using the above relations we calculate the bulk modulus, shear modulus, Young's modulus, and Poisson's ratio for Pd_2Ga. Their respective values are as follows: $B=178.69$ GPa, $G=59.31$ GPa $E=160.56$ GPa, and $v=0.354$.

It is known that the isotropic shear modulus and bulk modulus are measures of the hardness of a solid. The bulk modulus is a measure of resistance to the volume change by an applied pressure, whereas the shear modulus is a measure of resistance to the reversible deformation upon shear stress.[26] Therefore, the isotropic shear modulus is a better predictor of hardness than the bulk modulus. The isotropic shear modulus, a measurement of resistance to the shape change, is more pertinent to hardness and the larger shear modulus is mainly due to the larger C_{44}. The calculated isotropic shear modulus and bulk modulus are 59.31 and 178.69 GPa for Pd_2Ga. In general, the value of the shear modulus is an indication of the directional bonding between atoms. The degree of Cauchy violation ($C_{44}/C_{12}\neq 1$) indicates the deviation from a two-body central force model.[27] That is, the closer to 1 the C_{44}/C_{12} ratio is, the stronger the ionic character between two atoms is. In this work, the C_{44}/C_{12} ratio for Pd_2Ga is 0.48. This indicates that there is a strong ionic character of the bonding in Pd_2Ga.

According to the criterions in Refs. [26] and [28], a material is brittle (ductile) if the B/G ratio is less (greater) than 1.75. In fact, the value of B/G is greater than 1.75 for Pd_2Ga. Hence, this material behaves in a ductile manner.

The Young's modulus is defined as the ratio of stress to strain, and used to provide a measure of the stiffness of a material. The material is stiffer if the value of the Young's modulus is higher. Since the present value of the Young's modulus (160.56 GPa) for Pd_2Ga is relatively high, this material is stiff.

The value of the Poisson's ratio is indicative of the degree of directionality of the covalent bonds. This value is small ($v = 0.1$) for covalent materials, whereas for the ionic materials a typical value of v is 0.25.[29] The calculated Poisson's ratio is about 0.354 for Pd_2Ga. Therefore, the ionic contribution to the interatomic bonding for this compound is dominant. The lower and upper limits of v for central-force solids are 0.25 and 0.5, respectively.[30] For Pd_2Ga, the value of v is close to 0.35, indicating that the interatomic force is a central force.

Many low-symmetry crystals exhibit a high degree of elastic anisotropy.[31] The shear anisotropic factors in different crystallographic planes provide a measure of the degree of anisotropy of atomic bonding in different planes. The shear anisotropic factors are given by

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}}, \tag{8}$$

$$A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}}, \tag{9}$$

$$A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}}, \tag{10}$$

for the (100), (010), and (001) planes, respectively.

The calculated A_1, A_2, and A_3 for Pd_2Ga are as follows: $A_1 = 0.982$, $A_2 = 0.728$, and $A_3 = 1.1876$. A value of unity means that the crystal exhibits isotropic properties while values other than unity represent varying degrees of anisotropy. Therefore, it can be seen that Pd_2Ga exhibits low anisotropy in the (010) plane. Another way of measuring the elastic anisotropy is to give the percentages of anisotropy in the compression ($A_{\rm comp}$) and shear ($A_{\rm shear}$).[24,25,32] The compression and shear are defined as

$$A_{\rm comp} = \frac{B_{\rm V} - B_{\rm R}}{B_{\rm V} + B_{\rm R}} \times 100, \tag{11}$$

$$A_{\rm shear} = \frac{G_{\rm V} - G_{\rm R}}{G_{\rm V} + G_{\rm R}} \times 100. \tag{12}$$

For crystals, these values can range from zero (signifying the isotropy) to 100% (representing the maximum anisotropy). The percentages of anisotropy $A_{\rm comp}$ and $A_{\rm shear}$ for Pd_2Ga are calculated to be 0.065% and 2.36%, which demonstrates that the anisotropy in compression is low and the anisotropy in shear is high.

The Debye temperature is an important fundamental parameter closely relevant to many physical properties, such as the specific heat and the melting temperature. At low temperatures the vibrational excitation arises solely from acoustic vibration. Hence, at low temperatures the Debye temperature calculated based on the elastic constants is the same as that determined by the specific heat measurements. We have calculated the Debye temperature ($\theta_{\rm D}$) based on the elastic constants using the following common relation:[33]

$$\theta_{\rm D} = \frac{\hbar}{k}\left[\frac{3n}{4\pi}\left(\frac{N_{\rm A}\rho}{M}\right)\right]^{1/3} v_{\rm m}\,, \tag{13}$$

where $\hbar$ is Planck's constant, k is Boltzmann's constant, $N_{\rm A}$ is Avogadro's constant, 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 the average sound velocity.[34] $v_{\rm m}$ can be given by

$$v_{\rm m} = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{-1/3}, \tag{14}$$

where v_l and v_t are the longitudinal and transverse elastic wave velocities, respectively. They can be obtained from Navier's equations[35]

$$v_l = \sqrt{\frac{3B + 4G}{3\rho}}, \quad v_t = \sqrt{\frac{G}{\rho}}. \tag{15}$$

The values of $v_{\rm m}$, $v_{\rm l}$, and $v_{\rm t}$ in the present formulas are calculated to be 2633.74, 4883.19, and 2342.35 m/s, respectively. The calculated Debye temperature for Pd_2Ga is 321.81 K. Unfortunately, there are no theoretical and experimental results to be compared with them.

3.3. Electronic properties

For a better understanding of the electronic and optical properties of Pd_2Ga, an investigation into the electronic band structure would be useful. The electronic band structure of Pd_2Ga is calculated along the highsymmetry directions in the first Brillouin zone. Specifically, the band structures is calculated along the lines connecting the high-symmetry points S (1/2, 1/2, 0), Y (0, 1/2, 0), Γ (0, 0, 0), S (1/2, 1/2, 0), and R (1/2, 1/2, 1/2) in the $\boldsymbol{k}$-space. As shown in Fig. 1, no band gap exists in the band structures, and this band structure exhibits a metallic character.

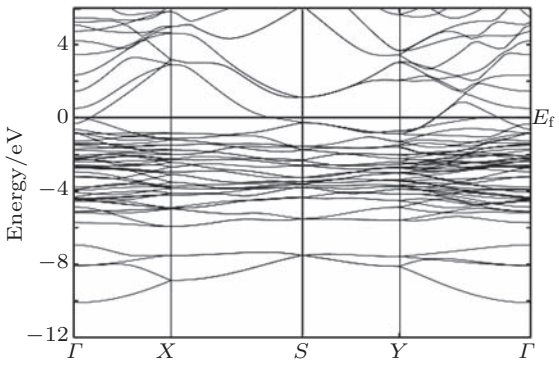


Fig. 1. The calculated electronic band structure of Pd_2Ga. The position of the Fermi level (E_f) is at 0 eV.

To understand the mechanical properties of Pd_2Ga on a fundamental level, the partial density of states (PDOS) is calculated at zero pressure via the density functional theory (DFT) method. The calculated results are shown in Fig. 2 along with the Fermi level. The position of the Fermi level is at 0 eV. In Fig. 1, the main components of the PDOS at the bottom of the conduction band are a mixture of the valance orbitals of Pd and Ga atoms. The states in the valance band from −10 to −7 eV are mainly composed of 4s (Ga) and 5s (Pd) states. The valance band elsewhere is dominated by the 4d (Pd) state. The 4s and 4p states of Ga atoms also contribute to the valance band, but their density is quite small compared with that of the 4d state of Pd atoms. From the quantitative analysis of the overlap extent between the 4d (Pd) and 4p (Ga) states, as shown in Fig. 1, we find that the overlap extent between two states are small. For this reason, we can conclude that Pd_2Ga has a high ionic character and small shear modulus.

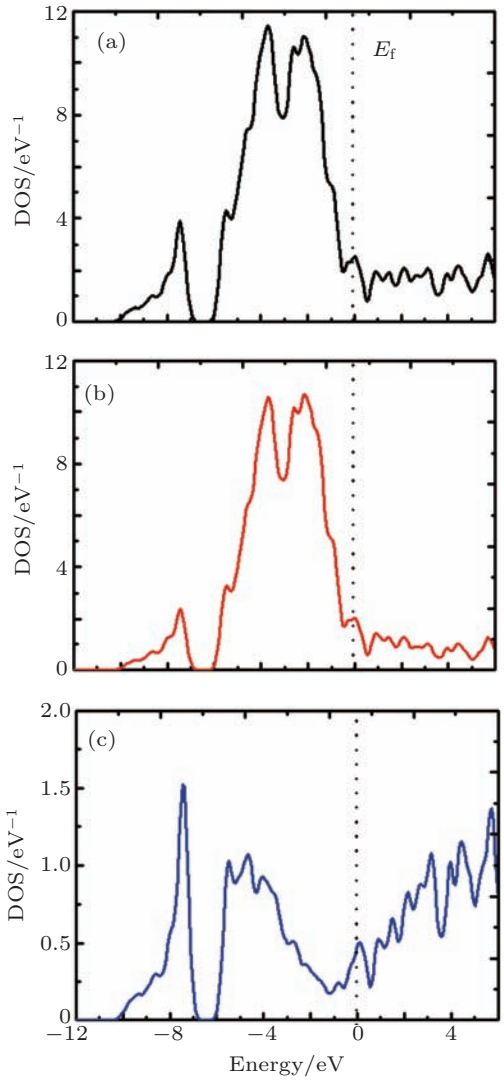


Fig. 2. (colour online) The total (DOS) and projected density of states for (a) Pd_2Ga, (b) Pd, and (c) Ga. The position of the Fermi level is at 0 eV.

3.4. Optical properties

It is well known that the role of the electric field vector ($\boldsymbol{E}$) of the incoming light is to polarize the material. At the level of linear response, the polarizability can be calculated using the following relation:[36]

$$P^i(\omega) = \chi^{(1)}_{ij}(-\omega, \omega) \cdot E^j(\omega), \tag{16}$$

where ω is the frequency of the electric field and $\chi^{(1)}_{ij}$ is the linear optical susceptibility tensor. $\chi^{(1)}_{ij}$ can be given by[37]

$$\begin{aligned}\chi^{(1)}_{ij}(-\omega, \omega) &= \frac{e^2}{\hbar\Omega}\sum_{nm\boldsymbol{k}} f_{nm}(\boldsymbol{k})\frac{r^i_{nm}(\boldsymbol{k})r^i_{mn}(\boldsymbol{k})}{\omega_{mn}(\boldsymbol{k}) - \omega} \\ &= \frac{\varepsilon_{ij}(\omega) - \delta_{ij}}{4\pi},\end{aligned} \tag{17}$$

where n and m denote the energy band, $f_{mn}(\boldsymbol{k}) \equiv f_m(\boldsymbol{k}) - f_n(\boldsymbol{k})$ is the Fermi occupation factor, Ω is the normalization volume, $\boldsymbol{r}_{nm}$ is the matrix element of the position operator,[37] and $\omega_{mn}(\boldsymbol{k}) \equiv \omega_m(\boldsymbol{k}) - \omega_n(\boldsymbol{k})$ is the frequency difference $\hbar\omega_n(\boldsymbol{k})$ is the energy of band n at wave vector $\boldsymbol{k}$. The dielectric function $\varepsilon_{ij}(\omega)$ can be derived from Eq. (19) as

$$\varepsilon_{ij}(\omega) = 1 + 4\pi\chi^{(1)}_{ij}(-\omega, \omega)$$

and its imaginary part ε^{ij}_2 can be given by

$$\begin{aligned}\varepsilon^{ij}_2(w) &= \frac{e^2}{\hbar\pi}\sum_{nm}\int \mathrm{d}\boldsymbol{k} f_{nm}(\boldsymbol{k})\frac{v^i_{nm}(\boldsymbol{k})v^j_{nm}(\boldsymbol{k})}{\omega^2_{mn}} \\ &\quad \times \delta(\omega - \omega_{mn}(\boldsymbol{k})).\end{aligned} \tag{18}$$

Its real part $\varepsilon^{ij}_1(\omega)$ can be obtained by using the Kramers–Kroning transformation.[37] Because the Kohn–Sham equations determine the property of the

ground state, the calculated unoccupied conduction bands have no physical significance.

The known sum rule[38] can be used to determine some quantitative parameters, particularly the effective number ($N_{\rm eff}$) of the valence electrons per unit cell, as well as the effective optical dielectric constant ($\varepsilon_{\rm eff}$), which contributes to the optical constants of a crystal at an energy of E_0. One can obtain an estimate of the distribution of oscillator strengths for both intraband and interband transitions by computing $N_{\rm eff}(E_0)$ according to

$$N_{\rm eff}(E) = \frac{2m\varepsilon_0}{\pi\hbar^2 e^2 N_{\rm a}} \int_0^{\infty} \varepsilon_2(E) E \,{\rm d}E, \qquad (19)$$

where $N_{\rm a}$ is the atomic density in a crystal, ε_0 is the static dielectric constant, and e and m are the charge and mass of an electron, respectively

Further information on the role of the core and semi-core bands can be obtained by computing the contribution that various bands make to ε_0. According to the Kramers–Kroning relations, we obtain

$$\varepsilon_0(E) - 1 = \frac{2}{\pi} \int_0^{\infty} \varepsilon_2(E) E^{-1} \,{\rm d}E. \qquad (20)$$

Therefore, we can define an effective dielectric constant, which represents a different meaning of the interband transitions from that determined by the sum rule (Eq. (22)), according to the following relation:

$$\varepsilon_{\rm eff}(E) - 1 = \frac{2}{\pi} \int_0^{E_0} \varepsilon_2(E) E^{-1} \,{\rm d}E. \qquad (21)$$

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 0 to E_0, i.e., by the polarization of the electron shells.

In order to calculate the optical response by using the calculated band structure, we choose a photon-energy range from 0 to 14 eV, and find that a photon-energy range from 0 to 5 eV is sufficient for most optical functions.

The Pd_2Ga compound with an orthorhombic structure is a biaxial optical system. For this reason, its linear dielectric tensors have three independent diagonal elements.

We first calculate the real and imaginary parts of the x- and z-components of the frequency-dependent linear dielectric function (ε), and the results are shown in Figs. 3(a) and 3(b). It can be seen that ε_1^x is equal to 0 at about 1.19 and 13.22 eV, whereas ε_1^z is equal to 0 at about 1.70, 4.07, 5.24, and 13.07 eV. The respective peaks of ε_2^x and ε_2^z appear at around 0.60 and 0.24 eV, which correspond to the optical transitions from the valence band to the conduction band.

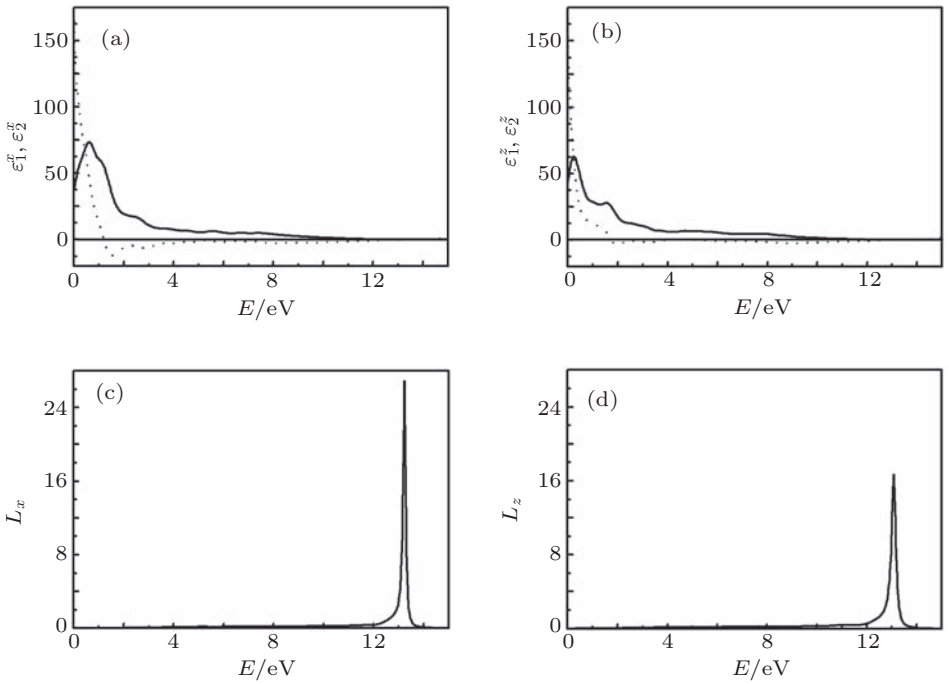


Fig. 3. The real (solid line) and imaginary (dashed line) parts of the x- (a) and z-components (b) of the dielectric function $\varepsilon = \varepsilon_1 - {\rm i}\,\varepsilon_2$ as functions of the photon energy. The energy-loss function L along the x- (c) and z-axes (d) as functions of the photon energy.

In general, there are various contributions to the dielectric function, and Fig. 3 only shows the contribution of the electronic polarizability. In the energy range from 0 to 1.8 eV, ε_1^z decreases with increasing photon energy, which signifies an anomalous dispersion. In this energy range, the transitions mainly occur between the occupied and unoccupied 4d states of Pb atoms, which can be seen in the DOS and PDOS displayed in Fig. 2.

The calculated energy-loss functions (L) are presented in Figs. 3(c) and 3(d), where L_x and $L_z$correspond to the x- and z-component. The function L describes the energy loss of the fast electrons traversing the material and the sharp maxima of L are associated with the existence of plasma oscillation.[39] The curves of L_x and L_z in Fig. 3 have a maximum near 13.22 and 13.07 eV for Pd_2Ga, respectively.

The calculated effective number of valence electron $N_{\rm eff}$ and the effective dielectric constant $\varepsilon_{\rm eff}$ are shown in Fig. 4. $N_{\rm eff}$ contributing to the interband transitions reaches the saturation value at about 12 eV. This means that the deep-lying valence orbitals participate in the interband transitions as well (see Fig. 1). $\varepsilon_{\rm eff}$ reaches the saturation value at about 2 eV. This means that the greatest contribution to $\varepsilon_{\rm eff}$ arises from the interband transitions between 0 and 2 eV.

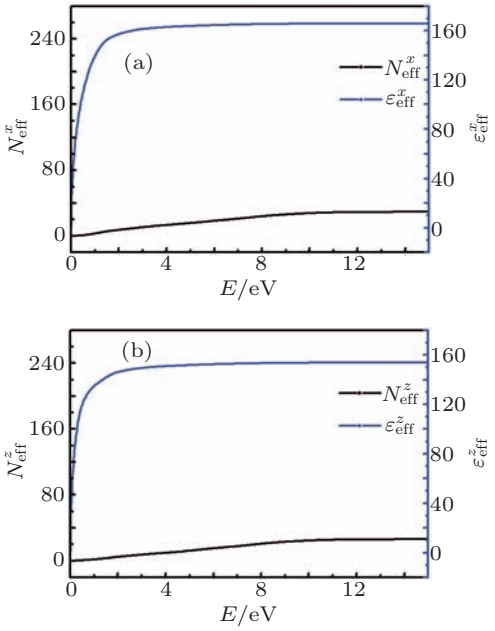


Fig. 4. (colour online) Energy spectra of $N_{\rm eff}$ and $\varepsilon_{\rm eff}$ along the x- (a) and z-axes (b) for Pd_2Ga.

3.5. Lattice dynamical properties

The phonon dispersion curves and phonon density of states have been calculated with the direct method[40] as is 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 to be 0.03 Å. To increase the precision and minimize the anharmonic effect, the positive and negative atomic displacements along the x, y, and z axe are taken into account.

The calculated phonon dispersion curves and the corresponding one-phonon DOS for Pd_2Ga along the high-symmetry directions are illustrated in Fig. 5. Unfortunately, there are no other theoretical or experimental results available to compare with the present work. The unit cell of Pd_2Ga contains 12 atoms, which give rise to 36 phonon branches containing 3 acoustic modes and 33 optical modes. The calculated phonon dispersion curves have no soft mode at any vectors, which confirms the stability of Pd_2Ga. In addition, strong coupling exists between low-frequency optical and acoustic phonons. As shown in Fig. 5, there are a few optical modes at the bottom of the optical phonon branch moving down toward the acoustic region along the ΓS, ΓZ, and ΓY directions.

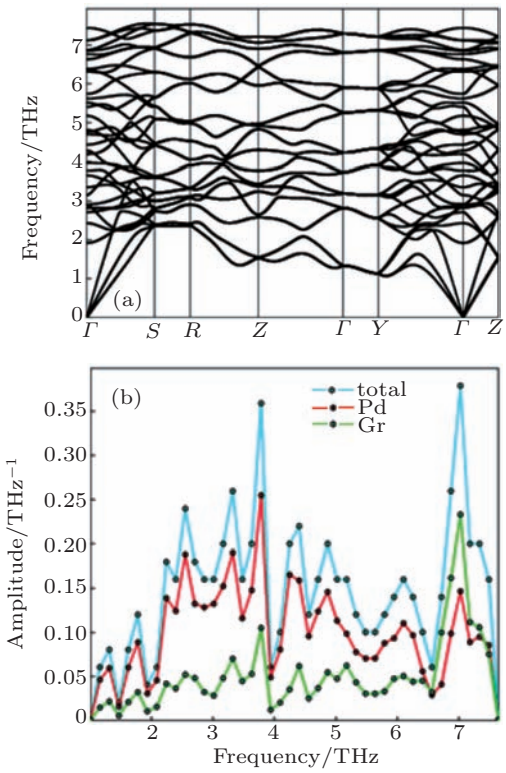


Fig. 5. (colour online) (a) Calculated phonon dispersion curves, (b) total and partial DOS.

The phonon dispersion curves on the right-hand side exhibit the corresponding total and partial DOS

for each compound. From the partial DOS of each displaced atom and the polarization vector analysis, it can be found that the phonon modes between 0 and 7 THz are essentially dominated by the motion of heavy Pd atoms. The Ga atoms make minor contribution to these phonon modes. The phonon modes between 7 and 8 THz are essentially dominated by the motion of light Ga atoms. In addition, the Pd atoms contribute to these optical phonon modes.

4. Conclusion

In the present work, we have investigated the structural, elastic, electronic, optical, and vibrational properties of the Pd_2Ga compound in detail by using the density functional methods. The elastic constants obtained using the volume-conserving technique show that this compound is mechanically stable. The relevant 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 revealed that the orthorhombic Pd_2Ga compound is in the ground-state configuration and the band structure of this compound is metallic in nature. We have examined the photon-energy dependent dielectric functions, some optical properties including the energy-loss function, the effective number of valance electrons, the effective optical dielectric constant, and the mechanical properties. The calculated phonon dispersion curves have no soft mode at any vectors, which confirms the stability of Pd_2Ga. Since there is no experimental data available for the elastic, electronic, and optical properties of Pd_2Ga, we believe that the *ab initio* theoretical estimation is the only reasonable tool for obtaining such important information.

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