First-Principles Study on Electronic, Magnetic, Optical, Mechanical, and Thermodynamic Properties of Semiconducting Gadolinium Phosphide in GGA, GGA+U, mBJ, GGA+SOC and GGA+SOC+U approaches

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Abstract

In the current article, the electronic, magnetic, and optical properties of GdP in the hypothetical zinc blende structure have been discussed by using GGA, GGA+U, mBJ, GGA+SOC, and GGA+SOC+U approaches. The energy vs volume plots in the three magnetic states suggest the ferromagnetic phase to be the stable phase of GdP. The cohesive energy calculated for GdP is negative, suggesting the stability of the compound. The electronic band structure calculations predict the binary GdP to be a direct bandgap conventional semiconductor. The optical properties confirm the semiconducting properties of GdP, and the bandgap formation follows Penn's criteria. The elastic constants also confirm the stability of the compound with ductile nature. The thermodynamic properties including Debye temperature, entropy, and specific heat capacity are studied under varying hydrostatic pressures taking into account the quasi-harmonic Debye model. The doping of Cu in the supercell of GdP results in the compound to exhibit half-metallic ferromagnetic properties. The magnetic moments calculated for $\text{Cu}_x\text{Gd}_{1-x}\text{P}$ ($x = 0.25$) are integer-valued backing its half-metallic character and fit excellent with the Slater-Pauling rule $Z_t - 8$. GdP in the zinc blende structure can prove a potential candidate for optoelectronic devices having better reflectivity in the UV region whereas its doped compounds have the potential to exhibit half-metallic properties useful in spintronics.

Keywords Conventional bandgap semiconductor · stable ferromagnetic phase · integer valued magnetic moments · follows Penn's criteria · stable mechanically · useful in optoelectronics and spintronics

1 Introduction

Semiconductors can be regarded as the elementary objects of modern electronics that have revolutionized and modernized life on earth as they form the important component of electronic devices. The group II–VI and group III–V compounds are well-known semiconductors that find a wide range of

interesting applications in electronics, device fabrication, and thin-film solar cells [1–4]. Apart from their unique electronic properties, semiconductors with excellent optical properties are considered to be novel candidates for various optoelectronic devices like light-emitting and laser diodes, Metal Insulator Semiconductor Photo-detectors, IC's, Electro-optic Waveguide Modulators, and heterostructure lasers [5–10].

In the existing electronic age, materials with designed properties have become very important for the development of multifunctional devices. Spintronics is an area established from materials that are regarded to be half-metals that use the spin of the electrons rather than focusing on their conventional charge property. The distinctive aspect of half-metal is that they are metals in one spin direction and semiconductors in the other. After the discovery of Heusler alloys in 1983 by de-Groot et al. [11, 12], half-metal ferromagnetic (HMF) materials have gained significant attention in recent years due to their broad application in spintronic fields such as magnetic

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sensors, tunnel junctions, spin-injectors and are attributed with the property of non-volatility [13–17]. Spintronic devices have an advantage over conventional electronic instruments in terms of non-volatility, increased transistor capacity, and data processing speeds [18].

As the conventional binary semiconductors, particularly Group III and V, are found to be stable in the zinc-blende (ZB) or rock salt (RS) structure, thus researchers considered the ZB and RS structures to search for binary half-metallic ferromagnetic compounds [19–23]. Apart from these binary compounds, doped compounds, oxides, DMS where a semiconductor is doped with a transition metal impurity, Heusler alloys, perovskites, ABO_3 type compounds, etc., have been reported to exhibit multiferroic or half-metallic properties [24–35].

The rare-earth elements became important members of the periodic table as their initial studies helped in bridging the gap between magnetism and quantum mechanics [36, 37] and recently have been investigated for advanced energy storage [38]. Zaoui et al. studied rare earth diborides and reported the hardness upon covalent bonding in these systems [39]. To look for the semiconductors having ferromagnetic ordering, rare earth compounds gained much attention during the 1960s [40–44], and among them, rare-earth monpnictides were investigated thoroughly because of their crystallization in the simple fcc structure [45–48]. Li et al. experimentally synthesized the various monpnictides of Gd by the mineralization method and reported GdP to behave as a semimetal having antiferromagnetic ordering at the Neel Temperature of 15.9 K [49]. Early works present the semiconducting nature of GdN whereas further investigations performed on Gd-based pnictides suggest that GdN exhibits half-metallic properties, and this half-metallicity is lost when one moves down the group of the pnictides. The reviews by Duan et al. and Petit et al. on rare earth pnictides and chalcogenides present much literature and work in the rock-salt type structure [50, 51]. Since all previous studies were based on considering the NaCl structure for GdP, so it will be interesting to study the electronic band structure, mechanical, optical, and thermodynamic properties of GdP in the zinc-blende structure and its doped compounds for their possible applications in the field of spintronics industry.

2 Method of calculations

By the first principles, the predictions of the structural, electronic, optical, and thermodynamic properties of the GdP compound were carried out by applying the Density Functional Theory (DFT) approach to Wien2k code [52, 53]. Exchange and correlation potentials were considered using Generalized Gradient Approximation (GGA) proposed by Perdew, Burke, and Ernzerhof [54], and for the corrections

to exchange-correlation due to the presence of f-electrons, Hubbard Model (U) and Tran Blaha modified Becke-Johnson (TB_mBJ) approach incorporated in full potential linearized augmented plane (FP-LAPW) method was used. We have used the scalar approximation for the valence states and for the core states full relativistic effects were considered. Monkhorst-Pack scheme [55] was used to perform the DFT and optical calculations by taking 1000k points dense mesh for the full Brillouin-zone integrations. The plane wave cut-off $RMT \cdot K_{\max}$ for the basic function was taken as 7.0 for energy convergence. The convergence to the self-consistent field equations is achieved within the energy of 10^{-4} Ry.

3 Results and discussions

3.1 Geometric structure and volume optimization

Before proceeding to any electronic or magnetic properties, it becomes very much important to check the stability of the compound in a particular structure to be investigated for, and as such energy is calculated as a function of lattice constants using the Murnaghan equation of state [56]. The WIEN2k package is provided with the volume optimization that determines the minimum (equilibrium) energy possessed by a system by plotting volume vs energy graphs. It is evident that any system tries to have minimum energy to achieve maximum stability, so we plotted energy vs volume graphs in the non-magnetic (NM), ferromagnetic (FM), and antiferromagnetic (AFM) phases of the binary rare earth pnictide GdP as given in Fig. 1(a–d). The ferromagnetic state of GdP is observed to have the least energy followed by AFM and NM phases, thus we predict the FM phase to be the most stable magnetic state.

While most of the studies on rare-earth GdP are performed in the NaCl type structure with space group Fm-3m 225 with Gd atoms located at (0 0 0) and P atoms at $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$. In the zinc blende structure (space group 216), though the Gd atom occupies the same (0, 0, 0) site, the P atom occupies $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ site Fig. 2(a). The optimized equilibrium lattice constant of GdP in the stable ferromagnetic state was calculated to be 6.36 Å. The ground state lattice constants in all three magnetic phases and their corresponding energies are reported in Table 1. To dope a transition metal impurity, an 8-atom supercell of GdP is created with $1 \times 1 \times 1$ dimensions shown in Fig. 2(b). One Gd atom located at (0 0 0) site is replaced by Cu accounting for 25% of the doping concentration.

To further confirm the stability of the compounds, the Cohesive energies (E_c) given in Table 2, were determined using the following equations,

$$E_{coh}^{GdP} = E_{tot}^{GdP} - (E_{Gd} + E_P) \quad (1)$$

Fig. 1 Volume optimization of GdP in (a–d) non-magnetic, ferromagnetic, and antiferromagnetic phases

$$E_{coh}^{GdPCu} = E_{tot}^{GdPCu} - (3E_{Gd} + 4E_P + E_{Cu}) \quad (2)$$

Where E_{tot}^{GdP} and E_{tot}^{GdPCu} are the total energies in the bulk form of the binary compound of GdP and the ternary doped $Gd_{0.75}PCu_{0.25}$ in the zinc-blende phase, E_{Gd} , E_P , and E_{Cu} are the total energies of isolated gadolinium, phosphorus, and copper, respectively. The cohesive energies were calculated to be negative in the ferromagnetic phase of GdP and Cu doped GdP that predicts the stability of the compound to be synthesized experimentally.

3.2 Electronic and magnetic properties

To study the ground state electronic and magnetic properties, spin-polarized DFT calculations are performed at the equilibrium lattice constant of GdP in GGA, GGA+U, mBJ, GGA+

SOC, and GGA+SOC+U approaches. The density of states and band structure plots of GdP reveal the semiconducting behavior of GdP having a direct bandgap nature shown in Fig. 3(a–c).

In the valence band of GdP, p orbitals of P have a remarkable contribution in the electronic states at the E_F in both the spin up and spin down channels. A small contribution due to d-Gd orbitals upon hybridization is also eminent in the same energy regions having the majority of the contribution due to triply degenerate d- t_{2g} (d_{xy} , d_{yz} , d_{xz}) states. Results of the GGA approach indicate that within the energy range of 1.4 eV to 3 eV, the contribution of the triply degenerated Gd d- t_{2g} states in the conduction band is dominant whereas, from 3 eV to higher energy 4.15 eV, doubly degenerate Gd d- e_g states dominate in the electronic band formation as disclosed in Fig. 4(A). A strong peak observed from -3.51 eV to -3.74 eV in the up spin channel that dominates in the

Table 1 Minimum equilibrium energy, equilibrium lattice constant, and Bulk modulus of GdP in NM, FM, and AFM phases

Compound	Phase	Equilibrium energy (Ry)	Lattice constant (Å)		B (GPa)
			Present (zinc-blende)	Others (rock-salt)	
GdP	NM	−23244.88368	6.31	5.704 [48] 5.709 [49]	45.079
	FM	−23245.4759	6.36	5.723 [57] 5.729 [48]	53.256
	AFM	−23245.02704	6.36		37.808

Fig. 2 Structure of (a) GdP and (b) $\text{Gd}_{0.75}\text{PCu}_{0.25}$ plotted using VESTA software

electronic bands is observed due to Gd-f orbitals as shown in the partial DOS plot of Fig. 4(D). In the down spin channel, the Gd-f orbitals have the maximum contribution in the electronic bands from 1.33 eV to 1.79 eV.

While employing the Hubbard correction term +U, Fig. 4(B, E), no major changes are observed in the electronic band structure and DOS plots as at the E_F in both the spin channels, a bandgap of 1.32 eV suggests the semiconducting behavior of GdP. In the up spin channel, from 1.36 eV to 3.08 eV, the electronic bands are observed due to triply degenerate Gd d_{t2g} orbitals, while the electronic bands having a width from 3.1 eV to 4.18 eV have the majority contribution of Gd d_{eg} orbitals. The electronic orbitals from the E_F in the up spin channel due to p-P orbitals have a width up to -2.11 eV, whereas Gd-f orbitals have the majority contribution from 3.6 eV to -3.79 eV in this spin channel. In the down spin channel, the electronic bands near the E_F to -2.02 eV are observed due to p-P orbitals. A strong peak that has the majority contribution as given in DOS and pDOS plots spanning from 1.38 eV to 1.8 eV is observed due to Gd-f orbitals.

GdP in the much accurate mBJ potential is observed to have an increased value of the bandgap of about 2.2 eV in the up spin channel whereas, in the down spin channel, the E_F is shifted up towards the CB that shifts the p-P bands below the E_F opening a bandgap of about 1.45 eV in this spin and has the tendency to exhibit half-metallic ferromagnetic properties. In the spin-up channel, the Gd- d_{t2g} orbitals are observed to span from 2.44 eV to 3.7 eV and after 3.7 eV doubly degenerate Gd- d_{eg} have the majority contribution in electronic states. In this particular spin channel, the p-P orbitals arise

from the E_F to -1.88 eV, while the more dominant f-orbitals span from -3.4 eV to -3.6 eV. In the down spin channel, the p-P states have a width from -1.87 eV to -0.048 eV that remain just below the E_F , while the Gd-f orbitals that span from 1.32 eV to 1.73 eV are located above the E_F are responsible for the formation of the bandgap of about 1.45 eV in this spin channel shown in Fig. 4(C, F). The band structures given in Fig. 5(a–f), clearly show the semiconducting behavior of GdP in GGA, GGA+U, and mBJ approaches.

The scalar relativistic effects are considered due to the presence of the heavy rare-earth element Gd by performing GGA+SO calculations. The band structures in both up spin and down spin channels given in Fig. 6(a,b) demonstrate the semiconducting behavior of GdP. More accurate GGA+SO+U calculations were performed to study the electronic properties of the GdP. The spin-orbit coupling interactions alongside the Hubbard parameter ($U_{\min} = 2\text{eV}$) are strong enough to dislocate the bands that otherwise were touching the E_F , below the E_F in both the spin channels thus evincing semiconducting properties. The bandgap in the up spin channel is observed to be around 1.36 eV, while in the down spin channel, the band is observed to be ~1.25 eV, Fig. 6(c,d).

In $\text{Gd}_{0.75}\text{PCu}_{0.25}$, the transition from semiconductor to half-metal is observed as in the down spin channel, the electronic bands cross the Fermi energy level, whereas in the up spin channel, a bandgap of about 1.7 eV is observed. The d-Cu and p-P orbitals in the up spin channel are pushed above the E_F in the CB that opens up a bandgap whereas in the down spin channel, the metallic properties can be attributed to the p-P orbitals that cross

Table 2 Cohesive energies of GdP and ternary $\text{Gd}_{0.75}\text{PCu}_{0.25}$

Compound	Gd	P	Cu	Total energy (Ry)	Phase	E_{COHESIVE} (eV)
GdP	-22561.1165	-653.9431	-	-23244.88368	NM	0.17597
				-23245.4759	FM	-0.41625
				-23245.02704	AFM	0.03261
$\text{Gd}_{0.75}\text{PCu}_{0.25}$	-22561.1165	-653.9431	-3310.0522	-73730.44638	FM	-121.271

Fig. 3 Total DOS of GdP in (A) GGA (B) GGA+U and (C) mBJ in both spin channels

the Fermi energy level. The f-states, being the semi-core states, are observed to contribute towards the electronic band formation away from the E_F at about 1.75 eV in the down spin channel. The Total DOS, Partial DOS, and band structure plots that predict the half-metallic properties in $\text{Gd}_{0.75}\text{PCu}_{0.25}$ are shown in Figs. 7, 8. The energy band gap of GdP and $\text{Gd}_{0.75}\text{PCu}_{0.25}$ is tabulated in Table 3.

The spin polarization is calculated by,

$$P = \frac{N_{\uparrow} - N_{\downarrow}}{N_{\uparrow} + N_{\downarrow}} \text{ (at the } E_F) \quad (3)$$

Where $N_{\uparrow}$ is the number of electronic states traversing the E_F in the up spin channel and $N_{\downarrow}$ is the number of electronic states that are crossing the Fermi level in the down spin channel. $\text{Gd}_{0.75}\text{PCu}_{0.25}$ is observed to exhibit 100% spin polarization like other half-metallic ferromagnetic materials that are known to exhibit 100% spin polarization at the Fermi energy level.

3.3 Magnetic properties

The spin-polarized calculations reveal the ferromagnetic ordering in the GdP. The PDOS indicates that the f-orbitals of Gd have maximum contribution towards the electronic states in the vicinity of the Fermi energy level; thus, we expect the Gd atom to have a major part in the total magnetic moments in GdP. Further, calculated magnetic moments of the individual atoms (Table 4) support the results of electronic properties. The total spin magnetic moments have a value of $6.99 \mu_B$ in GGA and GGA+U, while in mBJ potential, the magnetic moments of GdP show a change from non-integer to the integer value of $7 \mu_B$ and follow the Slater-Pauling rule of $M_t = Z_t - 8$ [58]. In GGA+SOC and GGA+SOC+U approaches, the magnetic moments are found to have a value of $6.95 \mu_B$. In mBJ potential, the P spins have the positive value of the magnetic moments that sum up to integer value of magnetic moments in GdP, whereas in all other approximations,

Fig. 4 Partial DOS of GdP in (A,D) GGA (B,E) GGA+U and (C,F) mBJ in both spin channels

Fig. 5 Band structure of GdP in (a,b) GGA, (c,d) GGA+U, and (e,f) mBJ in both spin channels

the magnetic moment of P atoms is negative that reveal the ferrimagnetic ordering of their magnetic states and can be attributed to the antiparallel alignment of the P spins than that of the Gd atom. In $\text{Gd}_{0.75}\text{PCu}_{0.25}$, the total spin magnetic moments had an integer value of $23 \mu_B$ and also fit excellent with the Slater-Pauling rule of $M_t = Z_t - 8$ as given in Table 5.

For binary GdP, we consider the semi-core f-orbitals also summing the total valence electrons to 15 and by applying the SP rule of $Z_t - 8$, the net magnetic moment becomes $7 \mu_B$. In the case of $\text{Gd}_{0.75}\text{PCu}_{0.25}$, as the supercell has been created,

we consider the outermost electrons for Gd as having 3 valence electrons; thus, the total valence electrons, $[(3 \times \text{valence electrons of Gd}) + (4 \times \text{valence electrons of P}) + (\text{valence electrons of Cu})]$ in the doped compound sum to 31 and again after applying the SP rule of $Z_t - 8$, the net magnetic moment sums to $23 \mu_B$ as observed in our case.

3.4 Optical properties

The forbidden energy range of semiconductors is a matter of great interest while optimizing, expanding, and enhancing

Fig. 6 Band structure of GdP in (a,b) GGA+SO, and (c,d) GGA+SO+U, in both spin channels

their applications. The energy needed to operate the optoelectronic devices strongly depends upon the band gap of semiconductors. For gaining deeper information about the optical behavior of compounds, it is necessary to analyze the complex dielectric function. Complex dielectric function is used to explore the response of materials on their interaction with EM waves along with the dissemination of EM waves in different mediums. It also provides information about electron-phonon interaction as well. Stored or absorbed energy in any medium is well explained by $\epsilon_1(\omega)$, which is the real part of dielectric function while this stored energy can be extracted from the

medium with the help of imaginary part of dielectric function $\epsilon_2(\omega)$ by imposing Kramer Krong transformation. $\epsilon_2(\omega)$ also explains band structures, absorption trend, and movement of charge carriers from valance band to the conduction band.

3.4.1 Dielectric function

The optical responsive nature of any medium can be calculated via a dielectric function which is given as $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. The real and imaginary parts, $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$, of the investigated compound GdP computed by applying various techniques, are given in Fig. 9(a,b). The most noteworthy measurement of $\epsilon_1(\omega)$ is the computation of zero frequency limit $\epsilon_1(0)$ as it robustly relies on bandgap and is the electronic constituent of static dielectric constant. The figure indicated the positive and negative sections of the real part of the dielectric function. The positive half is related to the propagation, while the negative half is related to the absorption of EM waves. Value of zero frequency limit $\epsilon_1(0)$ calculated with mBJ < GGA < GGA+U < GGA+SOC+U < GGA+SOC.

The static values of $\epsilon_1(0)$ for GdP in GGA, +U, mBJ GGA+SOC, and GGA+SOC+U approaches were calculated to be 8.38, 8.46, 6.92, 15.8, and 15.7, respectively. The other majority peaks are observed at 1.62 eV (value of 12), 2.98 eV (10.18), and 3.77 eV (6.7) in GGA; 1.56 eV (12.04), 2.92 eV (9.96), and 3.74 eV (6.66) in GGA+U, whereas in mBJ approach, the peaks are observed at 1.51 eV (9.22), 2.68 eV (8.41), and 3.77 eV (9.61). In the case of GGA+SOC, the majority peaks are observed at 1.8 eV (value of 22) and 3.1 eV (17) and in the GGA+SOC+U approach, the peaks obtained at 1.31 eV, 2.6 eV, and 3.3 eV have the values of 20.2, 15.5, and 18.2, respectively. The difference between the values of $\epsilon_1(0)$ computed by GGA and GGA+U is minor, and the same is observed for the remaining two approximations. This observation fits well with the results of electronic properties as the calculated bandgap is highest for mBJ. This result is also by Penn's criteria according to which

Table 3 Energy bandgap (in eV) of $\text{Gd}_{0.75}\text{PCu}_{0.25}$ in GGA, and GdP in GGA, GGA+U, mBJ, GGA+SOC, and GGA+SOC+U approaches

Compound	Method	Type		Bandgap (eV)	
		Spin up (↑)	Spin down (↓)	Spin up (↑)	Spin down (↓)
GdP	GGA	Semicond.	Semicond.	1.37	1.31
	GGA+U	Semicond.	Semicond.	1.32	1.32
	mBJ	Semicond.	Semicond.	2.22	1.45
	GGA+SOC	Semicond.	Semicond.	1.1	1.1
	GGA+SOC+U	Semicond.	Semicond.	1.36	1.26
$\text{Gd}_{0.75}\text{PCu}_{0.25}$	GGA	Semicond.	metal	1.7	-

Fig. 7 (a) Total DOS (b,c) partial DOS of $\text{Gd}_{0.75}\text{PCu}_{0.25}$ in both spin channels

band gap value is inversely related with the static dielectric constant and is given as [59].

$$\epsilon(0) \approx (\hbar\omega/E_g)^2 + 1 \quad (4)$$

Thus, the larger the static value of $\epsilon_1(0)$, the lesser will be the magnitude of the band gap formed. The positive part of $\epsilon_1(\omega)$ signifies that at minor energy range, GdP is conducting, while the negative part of $\epsilon_1(\omega)$ at elevated energy ranges depicts its insulating nature. $\epsilon_1(\omega)$ is observed to attain negative values after 4.47 eV and attains maximum negative values at 5.34 eV. For half-metals, the value of $\epsilon_1(\omega) < 0$ [60]; thus, GdP can be predicted to exhibit half-metallic properties.

The absorption of a photon is linked with $\epsilon_2(\omega)$ and it portrays the electronic properties of crystalline materials; the $\epsilon_2(\omega)$ spectra of GdP represent its peak value around 4 eV. Peaks depict the shifting of charge carriers from filled to empty bands. As there is a rise in energy, $\epsilon_2(\omega)$ starts reducing and approaches zero at approximately 13 eV. Further, the absorption spectrum of the investigated compound shows a minor peak in the visible energy range, and this behavior predicts GdP as a potential candidate for optoelectronic applications.

Fig. 8 (a,b) Band structure of $\text{Gd}_{0.75}\text{PCu}_{0.25}$ in both spin channels

3.4.2 Reflectivity and optical conductivity

Reflectivity helps assess that a substance can be used for shielding purposes as an anti-reflecting coating. The optical reflectivity plots given in Fig. 9(c) show that the static values of the reflectivity vary from 0.2 to 0.36 as we switch from mBJ to GGA+SOC and suggest that the reflectivity spectrum is minimum in the IR and the visible region whereas for higher energies, the reflectivity increases and has the peak values in the vacuum UV region. Furthermore, the reflectivity plots suggest the same behavior at Near UV, Mid UV, and Deep UV regions. The maximum reflectivity is observed at 11.88 eV in GGA and GGA+U having a peak value of 0.59, whereas, in mBJ, the reflectivity has a maximum value of around 0.64 obtained at 12.01 eV. In the GGA+SOC approach, the reflectivity peak is observed at 12.01 eV having a maximum value of around 0.77 and in the GGA+SOC+U approach, the peak is obtained at 11.44 eV having a maximum value of around 0.77, suggesting the zinc blende GdP to be an excellent reflector in the high energy Vacuum UV region.

Optical conductivity $\sigma(\omega)$ determines the ability of a medium to initiate a phenomenon of conduction as the electromagnetic radiations try to propagate through it. Fig. 9(d) portrays the optical conductivity graph of the zinc blende GdP and from the graph, it is clear that the conductivity increases as energy increases. Five different curves are plotted in the graph that presents the optical conductivities. The range of conductivity is given for 0–14 eV. The graph shows almost the same pattern for all cases, up to 4.07 eV, which is the maximum conductivity value for GGA and GGA+U methods. The conductivity peak observed in the mBJ approach is observed to be slightly shifted towards higher energies having a maximum value at 4.72 eV. In SOC and SOC+U approaches, the maximum conductivity peaks are obtained at 4.2 eV and 4.37 eV, respectively. It is observed that the maxima of reflectivity for every single approximation is located around 4 eV predicting GdP to be a suitable material for optoelectronics. Above 4 eV, optical conductivity starts reducing following an oscillatory trend and becomes zero for higher energy values.

Table 4 Total spin magnetic moments of GdP in GGA, GGA+U, mBJ, GGA+SOC, and GGA+SOC+U approaches

Compound	Individual magnetic moments (μ_B)					
	Site	GGA	GGA+U	mBJ	GGA+SO	GGA+SO+U
GdP	Interstitial	0.09	0.09	0.11	0.09	0.09
	Gd	6.94	6.94	6.87	6.89	6.90
	P	−0.04	−0.04	0.02	−0.03	−0.04
	Total	6.99	6.99	7.00	6.95	6.95

3.4.3 Refractive index and absorption coefficient

Another significant physical quantity that describes the optical properties of any particular material is its refractive index (n). A reduction in the speed as light passes from one medium to another raises its refractive index. A trend analogous to the real part of the dielectric function is seen in the refractive index plots as it is derived from $\epsilon_1(\omega)$. The static values of the refractive index in GGA, GGA+U, mBJ, GGA+SOC, and GGA+SOC+U methods were calculated to be 2.89, 2.9, 2.63, 3.97, and 3.96, respectively. It is also known that the refractive indices are inversely related to the bandgap, thus if (n) increases, the bandgap decreases [60]. This result is also following our calculations. Results of GGA and GGA+U disclosed that the maximum value of the refractive index ($n = 3.48$) exists in the visible region; however, in the mBJ approach, n has a maximum value of 3.31 that is near the UV region of the electromagnetic spectrum. In the case of GGA+SOC and GGA+SOC+U approaches, the maximum values of the refractive index are calculated to be 4.77 and 4.59 located in the visible region. The refractive index is observed to be maximum for all the methods in the IR, Visible and near UV regions whereas for higher energies, the refractive index of the binary zinc-blende GdP is observed to decrease as plotted in Fig. 9(e).

Absorption coefficient $\alpha(\omega)$ is the fundamental optical parameter that calculates the amount of energy absorbed by any material. It can be noted from the spectrum of the absorption coefficient given in Fig. 9(f) that there is no sharp peak of $\alpha(\omega)$ in IR and in the visible energy range which implies that GdP can conduct both visible and IR rays. Peaks become more prominent around 4 eV and go on increasing up to 11.1 eV, so the highest value of $\alpha(\omega)$ exists in the UV region. The absorption peaks are observed to shift to higher energies that correspond to the blue shift due to the decrease in the wavelength. The shift of peaks in mBJ potential to shorter wavelength regions can be attributed to the quantum confinement effect that can improve the optoelectronic properties of the materials.

3.5 Elastic properties

The elastic constants c_{ij} are essential components in defining the mechanical characteristics of the compounds. The temporary deformation of material on the application of some external force in various directions is measured as elasticity. The elastic constants are also related to the Debye temperature specified heat, thermal expansion, and Gruneisen parameters. The knowledge of the elastic constants plays a key role in certain practical uses related to the mechanical properties of a material, like load deflection, sound velocity, thermo-elastic

Table 5 Total and individual spin magnetic moments of $\text{Gd}_{0.75}\text{PCu}_{0.25}$ in GGA

Individual magnetic moments in $\text{Gd}_{0.75}\text{PCu}_{0.25}$		Magnetic moments (μ_B)
Interstitial		1.124
Sphere 1, Cu		0.311
Sphere 2, Gd		6.987
Sphere 3, Gd		6.985
Sphere 4, Gd		6.989
Sphere 5, P		0.151
Sphere 6, P		0.151
Sphere 7, P		0.151
Sphere 8, P		0.151
Total		23.00

Fig. 9 (a) Real part $\epsilon_1(\omega)$, (b) Imaginary part $\epsilon_2(\omega)$, (c) Reflectivity, (d) conductivity, (e) Refraction, and (f) Absorption Coefficient of GdP in GGA, GGA+U, mBJ, GGA+SOC, and GGA+SOC+U approaches

Table 6 Elastic constants C_{11} , C_{12} and C_{44} (in GPa) and Bulk modulus B (GPa), Young's modulus E (GPa), Shear modulus G (GPa), Poisson's ratio ν , Cauchy's pressure $C_P = C_{12} - C_{44}$, Anisotropy factor A , and the B/G ratio calculated for GdP (spin polarized)

Compound	C_{11}	C_{12}	C_{44}	B	E	G	ν	$C_{12} - C_{44}$	A	B/G
GdP	64.443	46.599	43.255	52.547	60.849	23.278	0.31	17.84	4.85	2.257

Table 7 Longitude sound velocity V_l (m.s^{-1}), Transverse sound velocity V_t (m.s^{-1}), Average sound velocity V_m (m.s^{-1}), Debye temperature θ_D (K), and melting temperature T_{melt} (K) calculated for GdP

Compound	V_l	V_t	V_m	θ_D	T_{melt}
GdP	4151.37	2190.79	2265.39	263.20	933.92 ± 300

tension, internal pressure, and fracture durability. Since GdP has a cubic symmetry, only three elastic constants are required as C_{11} ($=C_{22}=C_{33}$), C_{12} ($=C_{13}=C_{23}$), and C_{44} ($=C_{55}=C_{66}$). These three elastic constants satisfy the Born stability conditions ($C_{11} - C_{12} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$, $C_{12} < B < C_{11}$) thereby determine the mechanical stability of compounds [61, 62] and justify our values to be considered near to exact results.

The mechanical parameters like Shear modulus (G), Bulk modulus (B), and Young's modulus (E) of the present binary compound that describe the hardness of material have been calculated according to the Voigt–Reuss–Hill approximation [63–65] given by the following equations [66–69].

Voigt's shear modulus is given by

$$G_v = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \quad (5)$$

and Reusse's shear modulus by

$$G_R = 5C_{44} \quad (6)$$

Shear modulus is calculated as

$$G = \frac{G_v + G_R}{2} \quad (7)$$

The other parameters are given by,

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \quad (8)$$

$$E = \frac{9BG}{(3B + G)} \quad (9)$$

$$A = \frac{2C_{44}}{(C_{11} - C_{12})} \quad (10)$$

Fig. 10 (a) Debye temperature, (b) Bulk modulus, (c,d) Volume of GdP at different pressures

Fig. 11 (a,b) Specific heat C_v , (c,d) Gamma of GdP at different pressures

$$\nu = \frac{(3B-2G)}{2(3B+G)} \quad (11)$$

The ratio of “B/G” gives the ductility and brittleness of a compound and according to Pugh, the compound exhibits brittle character if the ratio is less than 1.75, and the compound shows ductile behavior if the ratio is higher than this limit. The ratio of B/G is calculated to be 2.26 for GdP that is higher than the brittle limit value, thus, showing ductile behavior. The ductile nature of a material can also be calculated from the positive value of Cauchy pressure obtained from $C_{12} - C_{44}$, while the negative value of Cauchy pressure gives the brittle nature of the material.

Anisotropy is another important property of solids by which the materials exhibit different properties in different directions of the crystal lattice. The value of the anisotropy factor deviating from unity suggests the anisotropic behavior of GdP. The nature of bonding in the material being central or non-central is determined by

the Poisson’s ratio (ν). Central forces are known to be present if the value of ν is between 0.25 and 0.50; however, $\nu = 0.25$ suggests the non-central type of bonding. The elastic parameters are tabulated in Table 6. T_m , the melting temperature at which the compound from its solid-state will change to the liquid state is calculated from the equation [70].

$$T_{\text{melt}} = [553 \text{ (K)} + 5.911 C_{11}] \pm 300 \text{ K} \quad (12)$$

3.6 Thermodynamic properties

Using the quasi-harmonic Debye model, the thermodynamic properties of binary GdP were investigated via Gibbs2 code [71]. The thermodynamic parameters such as Debye Temperature (θ_D) also computed from the elastic constants, specific heat capacity (C_v), Grüneisen parameter (γ), Entropy (S), and thermal expansion (α) were computed to determine

Fig. 12 (a,b) Entropy (S), and (c) Coefficient of thermal expansion of GdP at different pressures

their pressure and temperature dependence from 0 GPa to 40 GPa and from 0 K to 800 K, respectively.

Debye temperature (θ_D) is the temperature of the highest normal vibrational mode of a crystal. It is an important parameter that describes the behavior of heat capacity and provides a strong understanding of the effect of temperature on the properties of a solid. The vibration excitations occur mainly from acoustic vibrations at low temperatures. Therefore, the Debye temperature estimated from elastic constants is the same as that calculated from specific heat measurements at low temperatures. The Debye temperature calculated at 0 GPa and 273 K is found to be 260 K, whereas from the elastic constants, θ_D is estimated to be around 263.20 K (Table 7) using the following equations [72].

$$\theta_D = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{\frac{1}{3}} V_m \quad (13)$$

$$V_m = \left[\frac{1}{3} \left(\frac{2}{V_t^3} + \frac{2}{V_l^3} \right) \right]^{-\frac{1}{3}} \quad (14)$$

$$V_t = \sqrt{\frac{G}{\rho}} \text{ and } V_l = \sqrt{\frac{3B + 4G}{3\rho}} \quad (15)$$

The Debye temperature is found to increase to 481.6 K at the pressure of 40 GPa while the bulk modulus is found to increase from 52.7 GPa at 0 GPa to 197 GPa at 40 GPa given in Fig. 10(a). The rise in the Debye temperature at higher pressures can be attributed to the hardness of the material as the hard materials are known to possess larger Debye temperatures. The value of bulk modulus calculated from the elastic constants is found to be 52.6 GPa which is almost equal to the value obtained from the thermodynamic calculations in Fig. 10(b) using the Gibbs2 code.

Materials are well known to compress on the application of some external pressure and expand with increasing temperature as observed in Fig. 10(c,d), while for the increasing pressure and temperature, the reverse process is observed for the Bulk modulus. As the temperature starts rising to a higher value, the bulk modulus is found to decrease, while the increase in pressure is found to increase the value of the bulk

modulus which is a typical pattern for solids. This pattern shows an inverse relationship between the temperature of the material and its hardness.

A material's internal energy is related to its specific heat (C_v), which is the material's ability to absorb heat energy from the environment. At constant volume, we studied the effect of temperature and pressure on the C_v of GdP. Fig. 11(a,b) represents the variation of C_v with the increase in T and P . The figure suggests that the variation of temperature has a greater impact on the value of C_v than that of the pressure. Up to 200 K, C_v ascends exponentially following the Debye T^3 law that suggests more absorbance of heat energy, while up to 500 K, a gradual increase is seen. At higher temperatures (>600 K), the classical behavior of the Dulong-Petit limit is observed. The value of specific heat for GdP at ground state conditions is calculated to be $47.8 \text{ Jmol}^{-1}\text{K}^{-1}$, while at a higher temperature of 800 K, its value is found to be $59.7 \text{ Jmol}^{-1}\text{K}^{-1}$.

A dimensionless parameter called Grüneisen parameter γ defines the impact of volume change on the vibrational properties of the material taking into account the crystal volume and phonon energy. It is observed from Fig. 11(c,d) that at low pressures (fixed) of 0, 10, and 20 GPa, γ increases gradually, whereas it is least affected at higher pressures with the rise in temperatures. The pressure-dependent properties at fixed temperatures show a reverse effect as γ is observed to decrease when pressure increases.

Entropy (S) of GdP at the ground state conditions is calculated to be around $68.86 \text{ Jmol}^{-1}\text{K}^{-1}$. From Fig. 12(a,b), it can be estimated that the entropy increases with the increase in temperature but has a reverse effect as the pressure is increased as it decreases monotonically. The coefficient of thermal expansion (α) given in Fig. 12(c) determines the variation of the dimension of the material at given pressures with the temperature change. This function correlates with the inter-atomic distance, so that the inter-atomic distance increases as α decreases. Materials that have a higher value of melting points possess a low coefficient of thermal expansion. It is observed that up to 200 K, α rises exponentially showing the anharmonic effect of the Debye model and after that, the thermal expansion coefficient gradually increases. The value of the thermal expansion coefficient for GdP at zero pressure and 273 K is calculated to be $4.7 \times 10^{-5} \text{ K}^{-1}$.

4 Conclusion

Overall, we have predicted the semiconducting behavior of GdP, a rare-earth phosphide, using the tool of first-principles calculations. The volume optimization reveals the fascinating character of GdP being more stable in the ferromagnetic phase in the zinc-blende structure as the compound is known to be stable in the antiferromagnetic phase in the rock-salt structure. The electronic bands at the E_F reflect the semiconducting

properties of the compound in different approaches. By considering spin-orbit interactions into account as in the GGA+SOC+U approach, GdP shows a clear bandgap in both the spin channels as the electronic bands are pushed below the E_F in the valence band. The integer-valued total magnetic moment of $7 \mu_B$ is observed to have a greater contribution by the rare-earth atom Gd. GdP is observed to follow the Slater-Pauling rule of Z_t-8 for the net magnetic moments and Penn's model for the formation of the bandgap while investigating its optical properties. The absorption spectrum reveals the blue shift while considering the mBJ calculations. The elastic and mechanical parameters predict the stability of the binary GdP having ductile behavior. The results of thermodynamic calculations performed by Gibbs2 code are following the results obtained from elastic constants. The doped $\text{Cu}_{0.25}\text{Gd}_{0.75}\text{P}$ is observed to exhibit half-metallic ferromagnetic properties. The magnetic moments calculated for $\text{Cu}_x\text{Gd}_{1-x}\text{P}$ ($x = 0.25$) are integer-valued backing its half-metallic character and fit excellent with the Slater-Pauling rule Z_t-8 . The semiconducting and half-metallic behavior of GdP and its doped compounds, integer-valued magnetic moments, the spin polarization of 100% at the E_F , mechanical stability makes it a potential candidate for memory storage, computer-based devices, optoelectronic devices, and particularly for spintronics.

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