

Article

Electronic and Magnetic Properties of PdRSb ($R = \text{La-Lu}$) Heusler Compounds; A First-Principles Study

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Abstract

The structural, electronic, and magnetic properties of the PdRSb, usually also referred to as RPdSb, ($R = \text{La-Lu}$) semi-Heusler compound series have been systematically investigated using first-principles calculations based on Density Functional Theory (DFT). Our structural optimizations reveal that the cubic $C1_b$ A-type variant is the energetically most favorable and thermodynamically stable ground state across the entire series. The calculated equilibrium lattice constants follow the well-known lanthanide contraction trend, with the exception of the Yb-based compound, which displays an anomalous lattice expansion. Magnetic stability analysis demonstrates that the magnetism is highly localized at the rare-earth (R) sites and closely follows the progressive filling of the $4f$ shell, peaking at $7 \mu_B$ for PdGdSb, while PdLaSb, PdYbSb, and PdLuSb remain non-magnetic. Furthermore, our electronic structure calculations reveal a rich variety of behaviors: PdLaSb and PdLuSb behave as gapless semiconductors, while most of the magnetic compounds exhibit near half-metallic characteristics. Notably, PdCeSb is predicted to be a perfect half-metal with an integer magnetic moment of $1 \mu_B$. These findings highlight the significant chemical tunability of the PdRSb family, positioning them as promising candidates for future applications in spintronics and magnetoelectronics.

Keywords: Heusler compounds; first-principles calculations; electronic structure; magnetic materials; Slater–Pauling rule

1. Introduction

In the early twentieth century, German metallurgist Fritz Heusler achieved a significant breakthrough while investigating methods to enhance the electrical conductivity of steel [1,2]. His discovery of Cu_2MnAl revealed a compound with a face-centered cubic (f.c.c.) crystal structure—strikingly similar to that of foundational semiconductors like silicon and gallium arsenide. This finding established the “Heusler compounds,” a versatile class of materials characterized by diverse intermetallic compositions and exceptional physical properties, including robust ferromagnetism and high Curie temperatures [3–5]. Based on their specific atomic arrangements, this expansive family is categorized into four primary groups [4,6]: semi-Heusler (e.g., NiMnSb), full-Heusler (e.g., Co_2MnSi), inverse Heusler (e.g., Mn_2CoSi), and quaternary Heusler compounds (e.g., $(\text{CoFe})\text{TiSi}$).

Within the broader family of Heusler-related derivatives, ternary antimonides with the general formula RTSb or TRSb ($R = \text{rare earth}$; $T = \text{transition metal}$) represent a significant class of intermetallic compounds characterized by a high degree of structural and functional diversity [7,8]. Depending on the atomic radii and electronegativity of the constituent elements, these systems typically crystallize in several distinct structural



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archetypes, most notably the cubic MgAgAs-type (half-Heusler), the hexagonal LiGaGe- or CaIn₂-type, and the orthorhombic TiNiSi-type [7,8]. Compounds containing group 10 transition metals, such as the NiRSb and PtRSb series, have attracted considerable attention due to their multifaceted physical phenomena, which include complex magnetic ground states, Kondo-lattice behavior, and non-trivial electronic topologies [8]. Furthermore, these materials have emerged as prominent candidates for energy-harvesting applications, as seen in the high-temperature thermoelectric performance and high carrier mobilities reported for various RNiSb phases [9,10]. The chemical tunability inherent in these RTSb frameworks provides a versatile platform for engineering specific electronic and magnetic properties, setting the stage for a detailed investigation into the PdRSb subgroup.

Extensive experimental investigations into the PdRSb series have revealed a remarkable sensitivity of their physical properties to the choice of the rare-earth (*R*) constituent and the resulting crystal symmetry [11–23]. While many members of this family, such as YPdSb, ErPdSb, and HoPdSb, are reported to crystallize in the cubic MgAgAs-type half-Heusler structure (space group $F\bar{4}3m$), others, including PrPdSb, NdPdSb, GdPdSb, and TbPdSb, favor a hexagonal LiGaGe-type or NdPtSb-type arrangement (space group $P6_3mc$) [11–13]. Magnetic studies indicate that most PdRSb compounds with magnetic R^{3+} ions exhibit localized magnetism and undergo long-range antiferromagnetic ordering at low temperatures, typically below 20 K [11–13]. For instance, GdPdSb and TbPdSb order antiferromagnetically at 17 K and 2.5 K, respectively, whereas CePdSb has been identified as a rare ferromagnetic Kondo-lattice system with $T_C \approx 17$ K [17]. From a transport perspective, the series spans a spectrum from metallic behavior in hexagonal phases like GdPdSb to semi-metallic or narrow-gap semiconducting behavior in cubic analogues [14]. Notably, YPdSb and ErPdSb have attracted interest for their high carrier mobilities and significant Seebeck coefficients—reaching values as high as 150–200 $\mu\text{V/K}$ at room temperature—positioning them as promising candidates for p-type thermoelectric applications [18,21,22]. Recent studies on YPdSb have further explored the origin of its negative temperature coefficient of resistivity, attributing it to a complex interplay of two-channel conductivity and strong electronic disorder [23].

To complement the experimental findings, extensive computational studies—primarily based on density functional theory (DFT)—have been conducted to elucidate the electronic, thermoelectric, and thermodynamic nature of the PdRSb series. These investigations often employ the generalized gradient approximation (GGA) augmented with spin-orbit coupling (SOC) and, for compounds containing 4*f* electrons, the Hubbard *U* parameter (GGA + *U*) to accurately describe the localized rare-earth states [24,25]. Theoretically, cubic PdRSb compounds such as YPdSb and ErPdSb are frequently identified as indirect narrow-gap semiconductors, with calculated band gaps typically ranging between 0.16 and 0.25 eV [21,25]. Such band structures are characterized by low effective masses for hole-like carriers, which underpins the high carrier mobilities and large power factors predicted for p-type doping in YPdSb and LuPdSb [23]. Furthermore, comparative studies across the *MYSb* (*M* = Ni, Pd, Pt) series indicate that the substitution of the transition metal significantly tunes the band gap and transport coefficients, with Pd-based variants often exhibiting an optimal balance between electronic conductivity and the Seebeck coefficient [22]. Beyond electronic properties, first-principles phonon calculations and thermodynamic modeling have provided insights into the lattice stability and thermal expansion of these phases, highlighting the role of electronic disorder and structural puckering—particularly in non-centrosymmetric variants like LaPdSb and CePdSb—in shaping their multifunctional profiles [21,26].

Despite the extensive body of work on individual PdRSb members, a systematic theoretical survey across the entire lanthanide series remains essential to fully elucidate the

chemical trends and the role of 4*f*-electron filling in this family. The primary motivation of the present study is to provide a comprehensive first-principles investigation of PdRSb (*R* = La–Lu) compounds, assuming a consistent cubic MgAgAs-type structural framework to isolate the electronic effects stemming strictly from the *R*-site substitution. While many of these systems exhibit antiferromagnetic ground states at cryogenic temperatures, we focus here on their ferromagnetic configurations to explore their potential as functional materials at higher thermal regimes and to assess their suitability for spintronic or magneto-electronic applications. By systematically calculating the electronic band structures and magnetic moments across the complete series, we aim to establish a predictive map of their physical properties, thereby identifying optimal rare-earth constituents for future targeted experimental synthesis and device integration.

2. Computational Methods and Computational Details

The theoretical investigation of the studied materials was carried out within the framework of Density Functional Theory (DFT) [27,28]. We employed two complementary computational codes: QUANTUM ESPRESSO [29,30] and FPLO [31,32]. Both packages solve the Kohn–Sham equations but implement different numerical approaches regarding wavefunction representation and crystal potential treatment.

Initially, structural optimizations and equilibrium lattice parameter determinations were performed using the QUANTUM ESPRESSO package (version 6.4.1) [29,30]. This open-source code employs a plane-wave basis set and pseudopotentials to describe electron–ion interactions. This approach allows for a systematic convergence check via the kinetic energy cutoff while significantly reducing computational cost by treating core electrons through effective potentials rather than explicit calculation. We employed the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange–correlation functional [33], with electron–ion interactions described by Projector Augmented Wave (PAW) pseudopotentials [34]. To ensure consistent convergence, a plane-wave basis set was used with kinetic energy cutoffs of 80 Ry and 640 Ry for the wavefunctions and charge density, respectively. Brillouin zone integration was carried out using a $12 \times 12 \times 12$ Monkhorst-Pack *k*-point grid [35], combined with Marzari–Vanderbilt cold smearing (0.01 Ry). Variable-cell relaxations were executed via the BFGS (Broyden, Fletcher, Goldfarb, and Shanno) algorithm under zero external pressure [36], with a self-consistent convergence threshold of 10^{-8} and a mixing factor of 0.3. At this stage, all calculations were performed within a non-magnetic approximation.

The electronic and magnetic properties were analyzed using the FPLO (Full-Potential Local-Orbital) code (version 22.00-62) [31,32]. As an all-electron, full-potential method, FPLO expands crystal wavefunctions in a basis of overlapping, non-orthogonal local atomic orbitals, ensuring a precise and unified treatment of both core and valence electrons. This is essential for accurately capturing magnetic moments and fine electronic features in rare-earth systems [31,32]. Using the optimized structures from QUANTUM ESPRESSO as input, we performed scalar-relativistic calculations within the GGA-PBE framework [33]. Brillouin zone integration was conducted using a $20 \times 20 \times 20$ *k*-point mesh [35]. The quantization axis was set along the (0, 0, 1) direction, with convergence criteria defined at 10^{-6} , in units of the electron’s charge, for the charge density and 10^{-8} Hartree for the total energy. Both non-magnetic and collinear magnetic configurations were explored to evaluate phase stability and detailed electronic structures.

By combining the structural reliability of QUANTUM ESPRESSO with the high precision of FPLO’s all-electron local-orbital scheme, a comprehensive and consistent description of the PdRSb series was achieved. In the following discussion, all references to magnetic moments denote exclusively their spin component. Conventional DFT calcu-

lations typically fail to capture the orbital contribution to the magnetic moment. Even when spin–orbit coupling is explicitly included in first-principles frameworks, the resulting orbital moments remain negligible. This orbital component is quenched in transition-metal atoms due to crystal field effects, whereas it can be substantial for lanthanide elements

It should be noted that we have not employed the GGA + U scheme, despite its frequent use in studies involving lanthanide-based compounds. The GGA + U approach is not a universal functional; rather, it incorporates a semi-empirical Coulomb repulsion term (U) into the Hamiltonian to account for strong on-site correlations. This term shifts the electronic bands in a phenomenological manner, and its precise value depends heavily on the specific atomic species and its chemical environment [37]. Indeed, even for the same element, local symmetry can significantly influence the appropriate magnitude of U. Given the difficulty in determining U experimentally and the lack of established values for most elements, we opted to use a standard GGA functional to ensure a consistent and uniform treatment across the entire series [38].

3. Results and Discussion

3.1. Structural Properties

The semi-Heusler compounds investigated in this study generally crystallize in the cubic $C1_b$ structure [3,4]. As illustrated in Figure 1 using PdLaSb as a model system, this lattice comprises four interpenetrating fcc sublattices, one of which remains vacant. The distribution of the three constituent atoms across these four available sites gives rise to three distinct structural variants. The nomenclature used in the literature to describe these atomic sequences often varies. Figure 1 depicts the two most common conventions: The first convention (typical for half-metallic systems like NiMnSb) fixes the transition metal (Pd) at the A site while varying the positions of the remaining atoms (La and Sb). The second convention yields an identical atomic sequence along the body diagonal but is defined by keeping the D site consistently vacant. While all three $C1_b$ variants maintain overall tetrahedral symmetry, the specific chemical nature of the nearest-neighbor environments fundamentally modifies the underlying orbital interactions. As discussed in Section 1, bulk PdRSb compounds may favor alternative non-cubic symmetries; however, screening from the Open Quantum Materials Database (OQMD) indicates that several of these compounds actually exhibit a cubic ground state as discussed below. Consequently, the cubic phase remains a physically significant target, especially since modern synthesis techniques can stabilize these structures in 2D geometries, such as thin films and heterostructures.

The initial stage of our investigation involves determining the equilibrium lattice constants for all compounds across the three $C1_b$ structural variants, as described in Section 2. Figure 2 illustrates the evolution of these lattice constants as a function of the rare-earth element, *R*. With the exception of Yb, the lattice constants for all three variants decrease monotonically as the atomic number of the *R* element increases. This trend is a hallmark of the lanthanide contraction: although the 4*f* subshell is being filled, these electrons are highly localized and provide poor shielding of the increasing nuclear charge. Consequently, the outer electron shells experience a stronger effective nuclear attraction, resulting in a reduced atomic radius and a corresponding decrease in the lattice constant.

Yb is a well-known exception in the lanthanide series. All other elements in the lanthanide series have two electrons at the 6*s* states, one electron at the 5*d* states, and the population of the 4*f* states varies between zero for La and fourteen for Lu. All these states are close in energy but the 4*f* states are much more localized around the nucleus with respect to the 6*s* and 5*d* states. As a result they all behave like trivalent cations in intermetallic and ionic compounds. Following the same reasoning Yb should have two electrons at the 6*s* valence states, one electron at the 5*d* valence states, and thirteen electrons

at the $4f$ states. In reality, Yb is an exception: there is no charge at the $5d$ states, and all fourteen $4f$ states are occupied (there is no electron at the $5d$ states); Yb-based intermetallic and ionic compounds are extremely stable, and Yb behaves like a divalent cation Yb^{2+} due to the two electrons at the $6s$ states and not as a trivalent cation Yb^{3+} (sometimes it even behaves as a so-called “mixed-valent” cation having a valence between +2 and +3) [39]. The divalent cation has a much larger atomic radius than the trivalent cation and thus leads to the observed anomaly in the trends of the lattice constants [39].

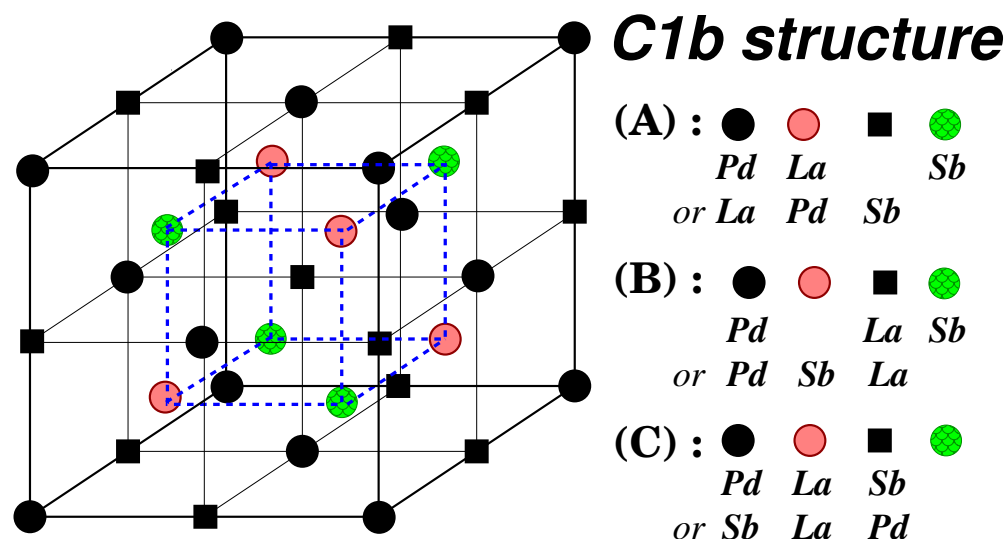


Figure 1. Schematic representation of the three structural variants of the $C1_b$ lattice in semi-Heusler compounds. For each variant, the two most common equivalent atomic sequences used in the literature are shown. The black spheres, pink spheres, black squares, and green spheres correspond to the A, B, C, and D Wyckoff sites, respectively. The large cube illustrated comprises four primitive unit cells.

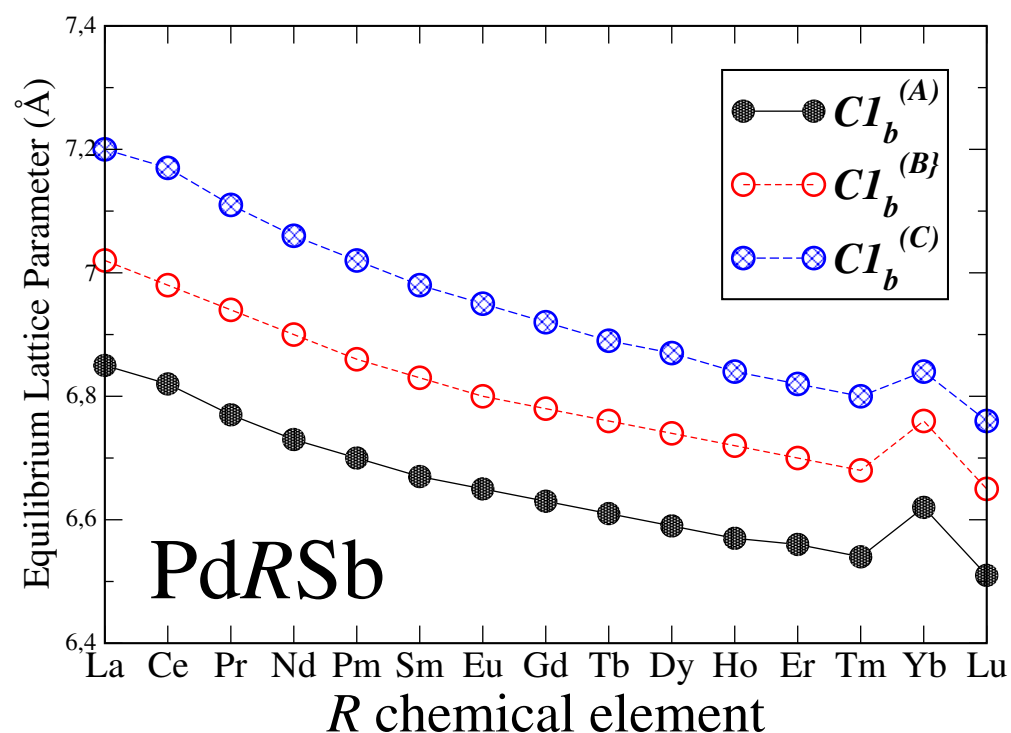


Figure 2. For all PdRSb compounds under study and for all three variants of the $C1_b$ lattice structure, we present the variation of the optimized equilibrium lattice constant as a function of the R atom.

The curves representing the three structural variants remain nearly parallel, maintaining a consistent offset of approximately 0.2 Å across the series. The A-type variant

consistently exhibits the smallest lattice constant, while the C-type is the largest. This persistent hierarchy stems from the distinct local coordination environments (see Figure 1). In the A variant, the *R* atoms are coordinated by four Pd atoms and four vacancies. In the B variant, the lattice expands as *R* forms a cubic framework with Pd. Finally, the C variant exhibits the greatest expansion, as the *R* atoms are closely coordinated by a full shell of four Pd and four Sb neighbors.

We next evaluate the relative stability of the magnetic versus non-magnetic states, alongside the energetic competition between the three $C1_b$ structural variants. Figure 3 presents the calculated energy differences between the non-magnetic and magnetic configurations for all 15 compounds. While the La-, Yb-, and Lu-based systems remain non-magnetic in all three phases, the remaining compounds favor a magnetic ground state. A noteworthy case is PdCeSb, which is non-magnetic in the B and C variants but becomes magnetic in the A variant. For this specific case, the energy gain from magnetism is only 0.024 eV per formula unit (f.u.), making it nearly indistinguishable on the provided scale. To determine the structural ground state, Figure 4 shows the total energy differences of the B and C variants relative to the A variant. In all investigated compounds, the positive energy differences confirm that the A variant is the most stable configuration. Interestingly, these differences remain remarkably consistent across the lanthanide series. The B variant lies approximately 1 eV above the A variant, while the C variant is further destabilized by an additional 1 eV relative to B. Given that these energy gaps (1 eV/f.u.) far exceed the room-temperature thermal energy ($k_B T \approx 0.025$ eV), the A variant is expected to be uniquely stable against thermal fluctuations.

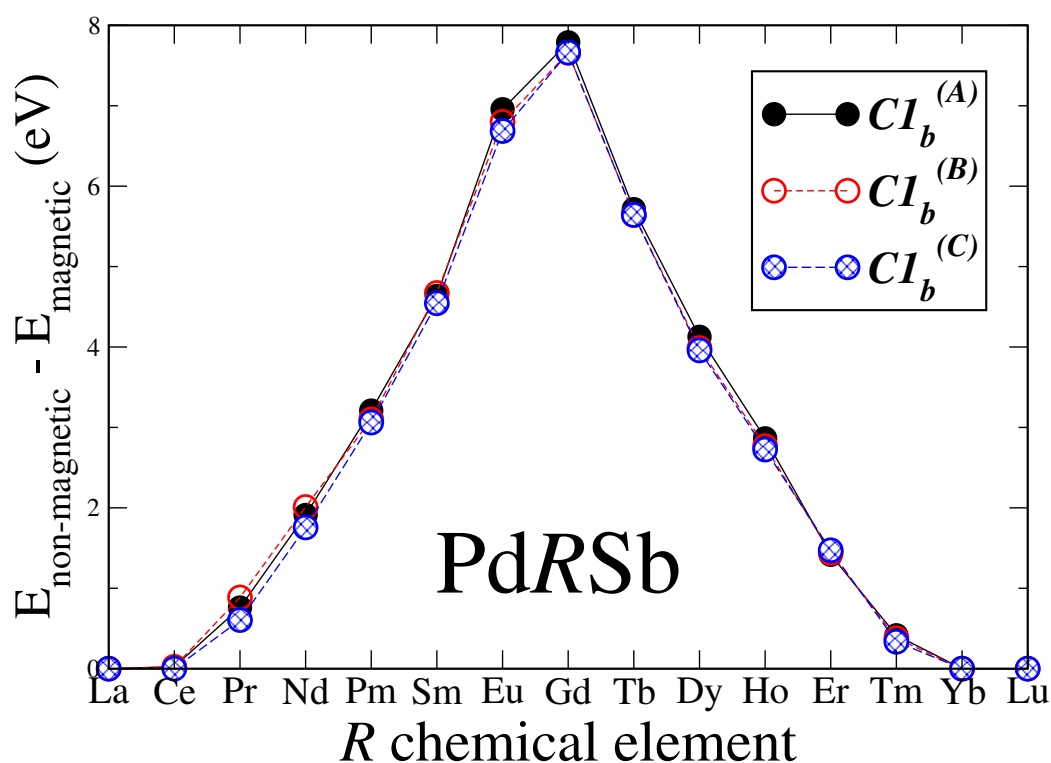


Figure 3. For all PdRSb compounds under study and for all three variants of the $C1_b$ lattice structure, we present the variation of the energy difference per formula unit between the non-magnetic and the magnetic calculations as a function of the *R* atom. A positive value means that the ferromagnetic state is the energetically favorable one.

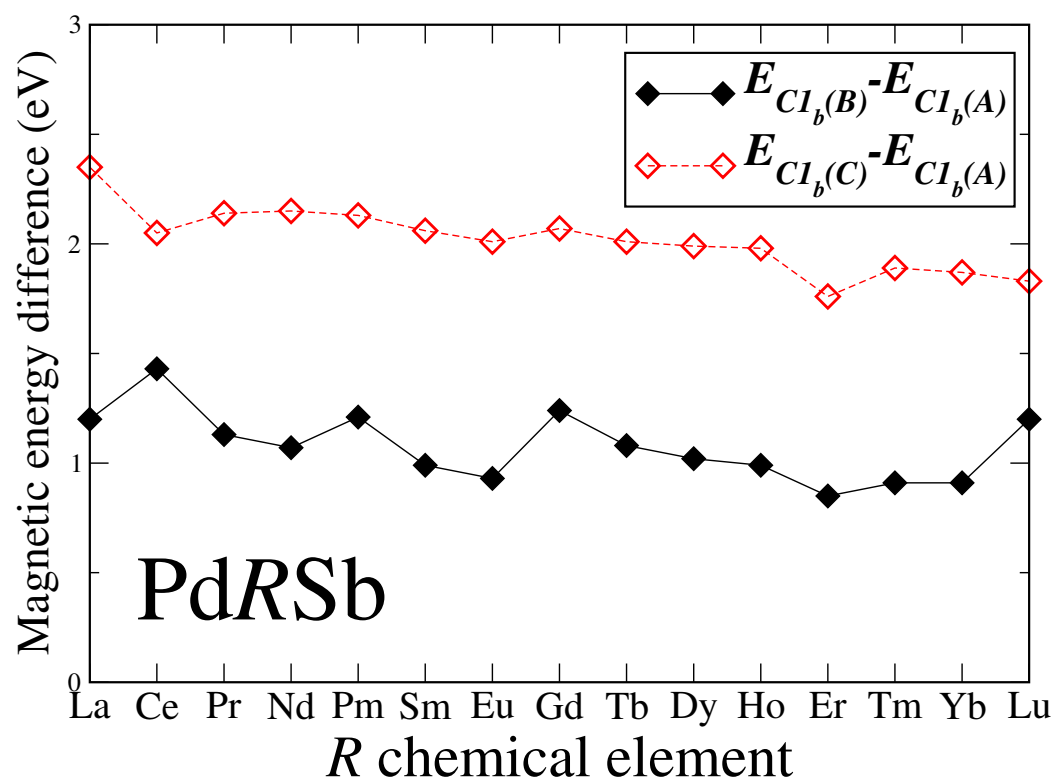


Figure 4. For all PdRSb compounds under study, we present the energy difference per formula unit between the B(C) variants of the $C1_b$ lattice structure and the A variant calculated at the equilibrium lattice constant of each variant. Note that for all compounds the A variant is the most stable, and the the C variant is the least stable.

3.2. Electronic and Magnetic Properties for the A Variant of the $C1_b$ Structure

Since the A-type structural variant is by far the most stable, we will now focus on this variant and study its properties. Table 1 summarizes the equilibrium lattice constants for all investigated compounds, which range from 6.51 to 6.85 Å. The final two columns provide a comparison with available data from OQMD, which aggregates thermodynamic first-principles calculations for an extensive library of compounds and crystal structures [40–42]. While all compounds exhibit significantly negative formation energies—exceeding 1 eV/atom—the most critical metric for experimental feasibility is the distance from the thermodynamic convex hull. This quantity represents the energy difference between the $C1_b$ phase and the most stable competing phases (or phase mixtures) at the same stoichiometry. For the majority of the compounds listed, the convex hull distance is exactly zero, identifying the $C1_b$ structure as the predicted ground state. In the cases of PdCeSb and PdYSb, the hull distances are notably small (less than 0.08 eV/atom), suggesting that these phases may be experimentally accessible at finite temperatures through thermal stabilization.

Figure 5 illustrates the evolution of the total spin magnetic moment per formula unit (f.u.) in units of μ_B as a function of the rare-earth element, R. All three structural variants exhibit nearly identical total moments, with the notable exception of PdCeSb; for this compound, only the A-variant possesses a magnetic state ($1 \mu_B$). For the remaining A-type compounds, the calculated moments align closely with the ideal values, assuming that only the 4f states contribute to the magnetic properties, represented by the dashed red line, with the exception of PdYbSb. The magnetic trend follows the progressive filling of the 4f shell: from PdLaSb to PdGdSb, the total spin magnetic moment increases linearly from 0 to $7 \mu_B$. Beyond the Gd-based compound, although the 4f occupancy continues to increase, the net spin imbalance decreases according to Hund's rules. This trend culminates in PdLuSb, which exhibits a zero magnetic moment due to its fully occupied $4f^{14}$ subshell.

PdYbSb is an exception in the observed trends as mentioned above since it has no electron at the $5d$ states, unlike all other lanthanide-series atoms which have one electron at the $5d$ states, and all its fourteen $4f$ states are occupied similarly to Lu.

Table 1. For all PdRSb compounds under study and for the A variants of the $C1_b$ lattice structure, we present the optimized equilibrium lattice constant in Å and the calculated atomic and total (per formula unit) spin magnetic moments in μ_B a function of the R atom. The ideal values of the total spin magnetic moments assume a strictly localized atomic-like behavior for the R -site $4f$ valence electrons, neglecting any potential hybridization with orbitals of the neighboring atoms. In the last two columns, we present, where available, the formation energy E_{form} , and the convex hull distance E_{hull} per atom for the cubic $C1_b^{(A)}$ lattice structure (all data are taken from the Open Quantum Materials Database [40–42]).

$C1_b^{(A)}$	a	m^{Pd}	m^R	m^{Sb}	$m^{\text{f.u.}}$	m^{ideal}	E_{form}	E_{Hull}
PdLaSb	6.85	0	0	0	0	0		
PdCeSb	6.82	−0.003	0.995	0.008	1.000	1	−1.137	0.015
PdPrSb	6.77	−0.060	2.176	−0.091	2.026	2	−1.094	0.000
PdNdSb	6.73	−0.0072	3.377	−0.124	3.181	3		
PdPmSb	6.70	−0.099	4.451	−0.181	4.171	4	−1.119	0.000
PdSmSb	6.67	−0.070	5.620	−0.127	5.423	5	−1.121	0.000
PdEuSb	6.65	−0.054	6.737	−0.130	6.552	6		
PdGdSb	6.63	−0.024	7.100	−0.076	7.000	7	−1.133	0.000
PdTbSb	6.61	0.005	5.948	−0.025	5.928	6		
PdDySb	6.59	0.019	4.787	0.003	4.809	5	−1.131	0.000
PdHoSb	6.57	0.016	3.762	0.001	3.779	4	−1.127	0.000
PdErSb	6.56	0.022	2.613	0.016	2.651	3		
PdTmSb	6.54	0.041	1.472	0.066	1.579	2	−1.113	0.000
PdYbSb	6.62	0	0	0	0	1	−0.911	0.078
PdLuSb	6.51	0	0	0	0	0		

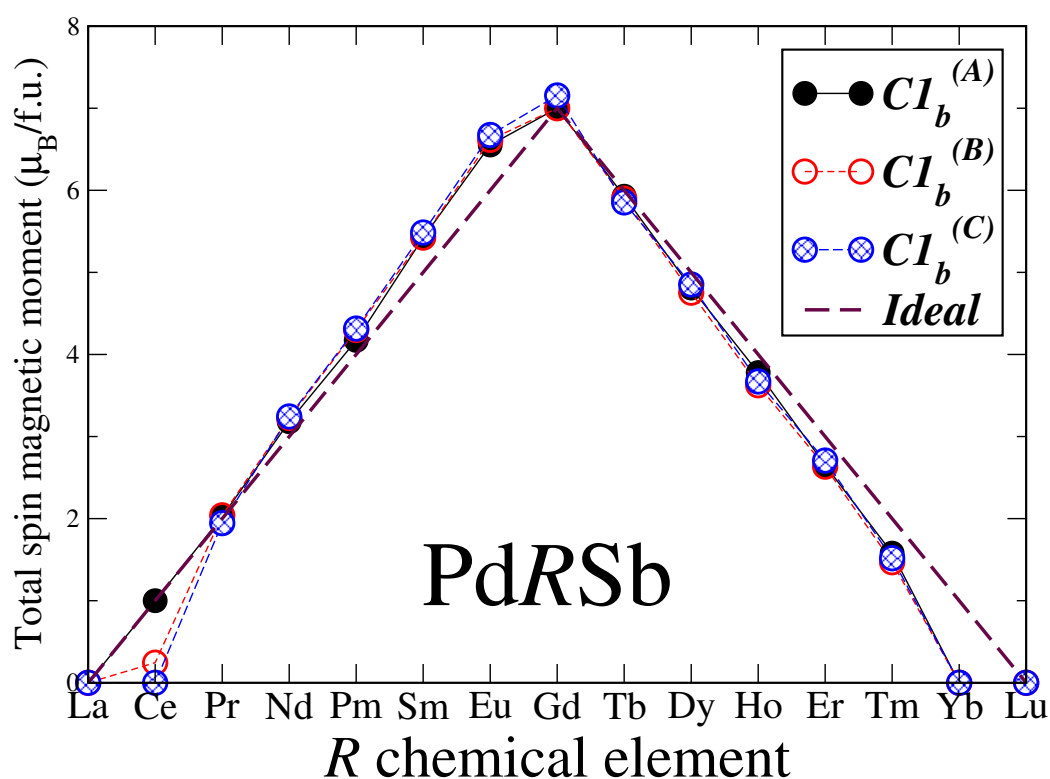


Figure 5. For all PdRSb compounds under study and for all three variants of the $C1_b$ lattice structure, we present the variation of the total spin magnetic moment per formula unit as a function of the R atom. The ideal values correspond to the case where the magnetism is completely localized at the R atoms.

The behavior of the total spin magnetic moments suggests that the magnetism originates primarily from the lanthanide elements, where it is expected to exhibit a highly localized character. To further investigate this behavior, we summarize the atomic and total spin magnetic moments in Table 1. The spin charge density is predominantly concentrated at the lanthanide sites, whose moments dominate the total magnetism of the system. As Pd is a $4d$ transition metal and Sb is a p -block metalloid, they do not exhibit intrinsic magnetism; instead, they carry marginal induced spin magnetic moments. These induced moments are one to two orders of magnitude smaller than those of the lanthanides. This disparity stems from the highly localized nature of the $4f$ valence states, which leads to negligible hybridization with the valence states of the neighboring Pd and Sb atoms. As we will discuss later the valence states of the Pd and Sb atoms can hybridize only with the $5d$ states of the lanthanide atoms.

The total DOS per formula unit presented in Figure 6, reveals that PdLaSb and PdLuSb behave as gapless semiconductors, a consequence of their empty and fully occupied $4f$ shells, respectively. In contrast, PdYSb exhibits conventional non-magnetic metallic behavior, consistent with its 14 valence electrons. Interestingly, the remaining compounds in the series exhibit near-half-metallicity. For these materials, an energy gap appears in the minority (spin-down) channel when the number of valence electrons is less than seven, while it shifts to the majority (spin-up) channel for the heavier lanthanides [43]. The degree of half-metallicity is closely tied to how closely the total spin magnetic moment approaches the ideal integer value (see Table 1). For instance, PdCeSb—with a moment of exactly $1 \mu_B$ —displays perfect half-metallicity. When the calculated moment exceeds the ideal value, a surplus of majority-spin states occurs. To maintain the integral total number of valence electrons, the Fermi level shifts below the energy gap, consequently leading to a reduction in the degree of spin polarization.

The R -resolved DOS presented in Figure 7 clearly illustrates the evolution of the $4f$ states across the series. In PdLaSb, the $4f$ spectral weight is negligible near the Fermi level, whereas in PdLuSb, the $4f$ shell is fully occupied and resides deep within the valence band, approximately 6 eV below the Fermi level. Moving from PdCeSb to PdEuSb, the occupied $4f$ states are predominantly located in the spin-up channel, with vanishing spectral weight in the spin-down states. PdGdSb serves as the transition case, where the seven spin-up states are entirely occupied, while the seven unoccupied spin-down states form a narrow, localized peak just above the Fermi level. From PdTbSb to PdTmSb, the spin-up channel remains filled, and additional electrons begin to populate the spin-down states. Notably, PdYbSb represents a singularity in the series: with fourteen $4f$ valence electrons and no $5d$ electrons as discussed above, it is non-magnetic, and its Fermi level intersects a prominent DOS peak. This electronic configuration explains the anomalous behavior of the lattice constant previously discussed in Section 3.1.

Finally, we examine the bonding characteristics of these compounds, using PdPrSb as a prototype. Figure 8 displays the orbital- and atom-resolved density of states (DOS). Note that the Pr $6s$ and Sb $5s$ states are localized near -10 eV and fall outside the energy range shown. The Pd $4d$ states are primarily located between -4 eV and -0.5 eV, a region that also encompasses the valence Sb $5p$ and Pr $5d$ states (the latter accommodating approximately one electron). Regarding the Pr $4f$ states, the absence of spin-down weight below the Fermi level, combined with the occupation of two electrons in the spin-up channel, yields a total calculated spin magnetic moment of $2 \mu_B$. These $4f$ states are energetically well separated from the remaining valence states, which exhibit negligible magnetization. This is consistent with expectations: the Pr $4f$ states are highly localized and do not participate in bonding. Instead, bonding arises from the hybridization of the more delocalized Pr $5d$, Pd $4d$, and Sb $5p$ orbitals. Since these valence orbitals transform according to the same

irreducible representations, they hybridize effectively within this energy window to form interatomic bonds.

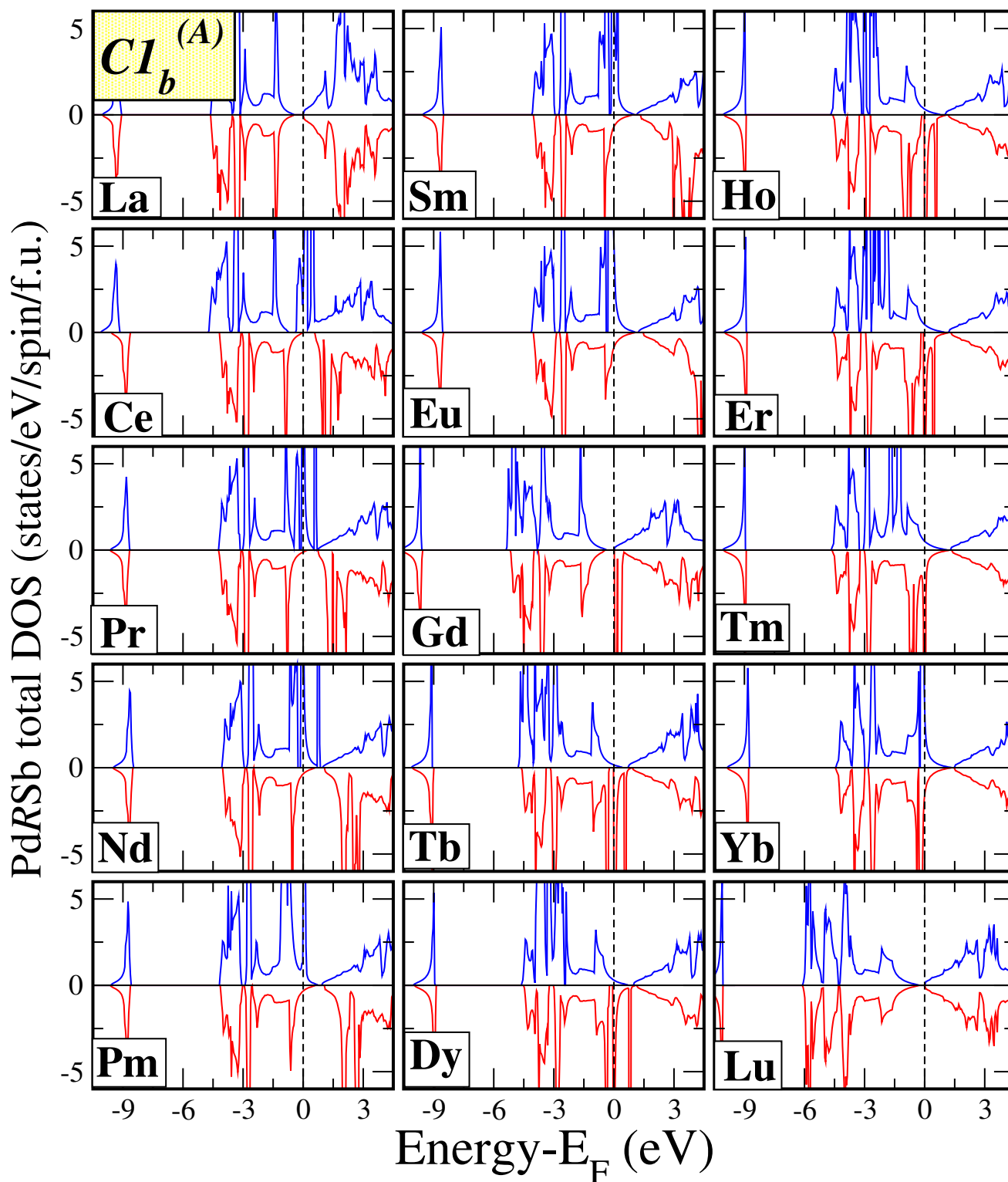


Figure 6. Total density of states (DOS) for PdRSb compounds using the PBE functional for the A variant of the $C1_b$ lattice structure which is the ground state. Positive (negative) DOS values correspond to the majority (minority)-spin electronic band structure. The zero energy values is set to be the Fermi level.

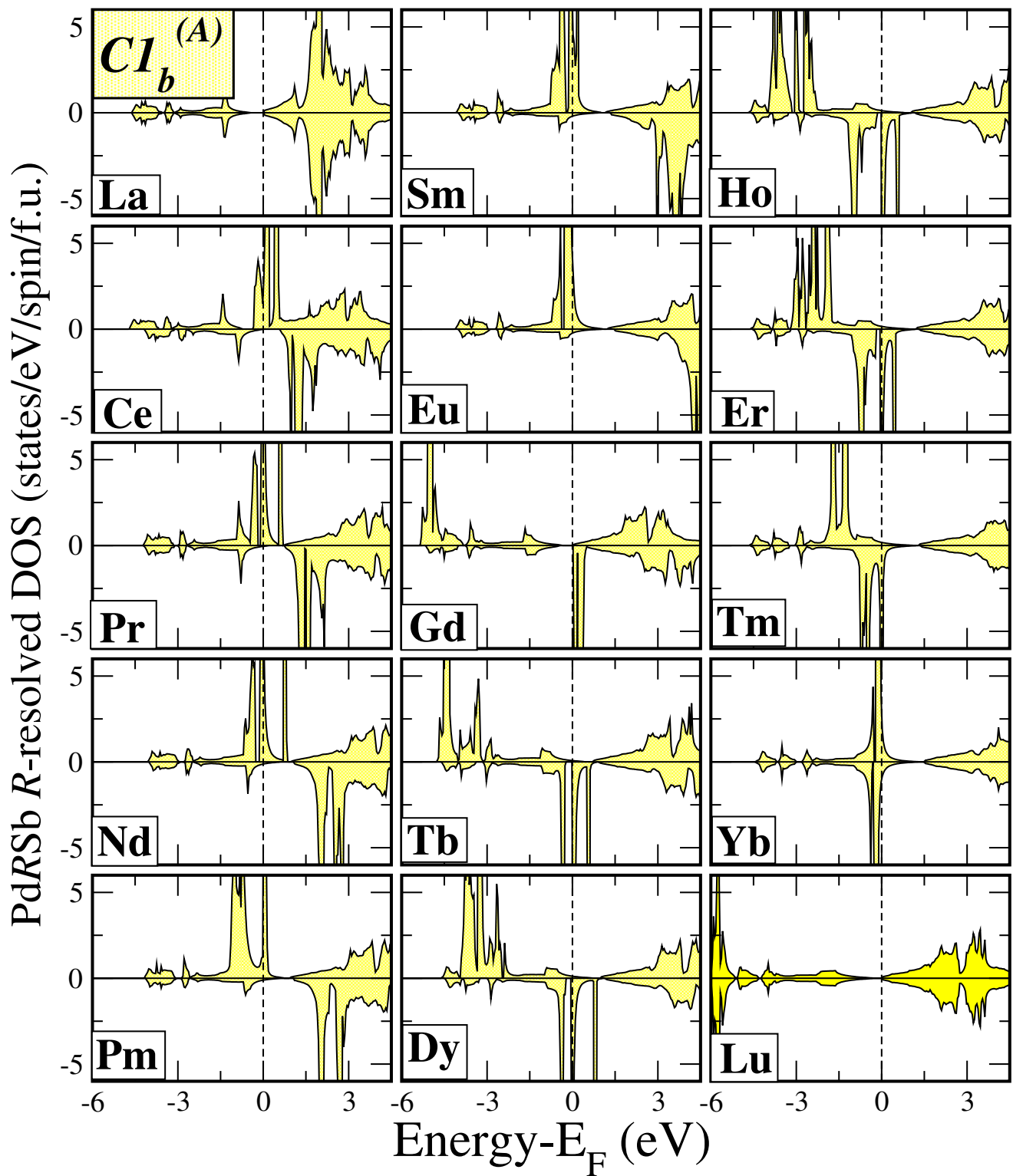


Figure 7. *R*-resolved density of states (DOS) for all PdRSb compounds using the PBE functional for the A variant of the $C1_b$ lattice structure which is the ground state. Details as in Figure 6.

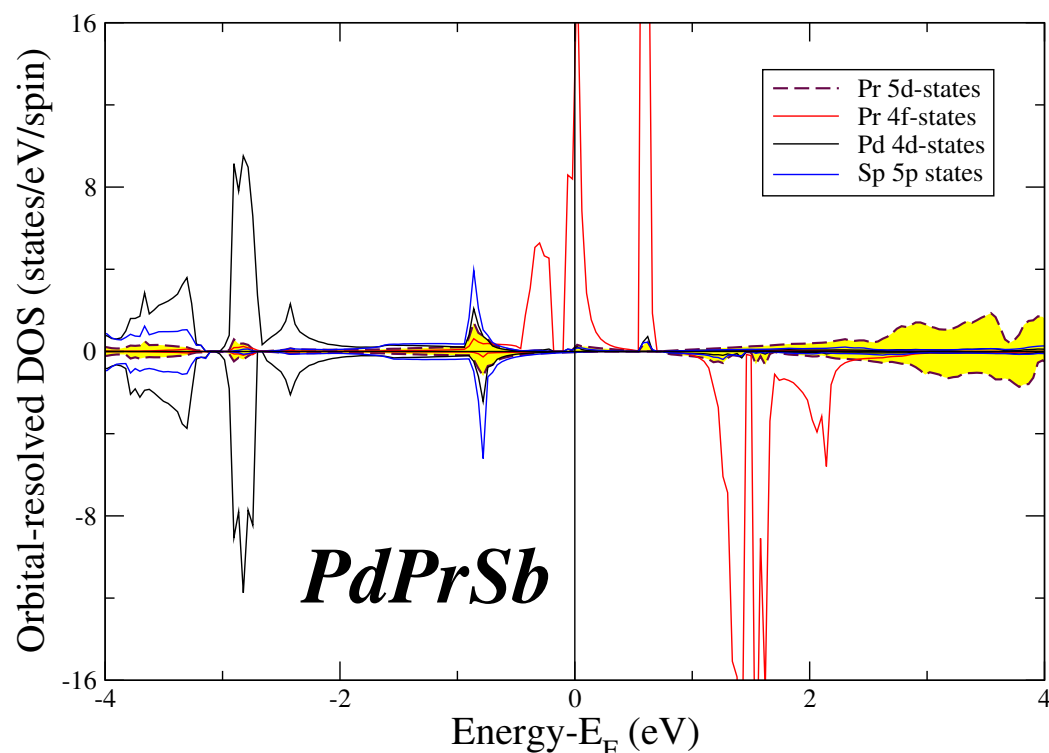


Figure 8. Orbital- and atom-resolved DOS for PdPrSb compounds using the PBE functional for the A variant of the $C1_b$ lattice structure which is the ground state. Details as in Figure 6.

4. Summary and Conclusions

In summary, we have performed a comprehensive first-principles investigation of the structural, electronic, and magnetic properties of the PdRSb ($R = \text{La-Lu}$) semi-Heusler compounds using DFT methodologies. Calculated formation energies and convex hull distances in the Open Quantum Materials Database confirm the strong thermodynamic stability of these Heusler phases [40]. Our key findings are as follows:

- **Structural Stability:** Among the three possible variants of the cubic $C1_b$ lattice, the A-type variant is universally the most energetically stable ground state for all R elements.
- **Lattice Trends:** The lattice constants decrease monotonically with the increasing atomic number of the rare-earth element, accurately reflecting the lanthanide contraction, with the non-magnetic PdYbSb serving as a notable singularity.
- **Magnetic Behavior:** The magnetic properties are driven by the localized $4f$ electrons of the rare-earth elements. Spin magnetic moments closely follow Hund's rules, reaching a maximum of $7 \mu_B$ per formula unit for PdGdSb. The transition metal (Pd) and metalloid (Sb) carry only negligible induced moments due to the highly localized nature of the rare-earth $4f$ states.
- **Electronic Properties:** The calculated density of states (DOS) reveals a diverse range of electronic behaviors. PdLaSb and PdLuSb act as gapless semiconductors, corresponding to their completely empty and fully occupied $4f$ shells, respectively.
- **Half-Metallicity:** While most magnetic members of the series exhibit near half-metallicity, PdCeSb stands out as a perfect half-metal with a well-defined gap in the minority-spin channel and an exact integer magnetic moment.

These theoretical insights establish a robust predictive map for the physical properties of the PdRSb series. The transition from non-magnetic semiconductors to half-metallic ferromagnets through simple rare-earth substitution demonstrates the exceptional tunability of this material family.

We expect these results to motivate targeted experimental synthesis and to pave the way for the integration of PdRSb compounds into next-generation spintronic, thermoelectric, and magneto-electronic devices.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

DFT	Density Functional Theory
DOS	Density of States
f.u.	Formula Unit
FPLO	Full-Potential Nonorthogonal Local-Orbital Minimum- Basis Band Structure Approach
GGA	Generalized Gradient Approximation
PBE	Perdew Burke Ernzerhof

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