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Pressure Induced Electronic Transitions in Rare Earth Compounds: A Pathway to Novel Superconducting Phases

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ABSTRACT
High-pressure conditions are known to significantly alter the electronic structures and superconducting behaviors of rare-earth compounds. This study focuses on pressure-induced electronic and structural transitions in selected neodymium-based compounds (NdP, NdAs, NdSb, NdBi) using a combination of high-pressure experimental techniques and first-principles calculations. Key phenomena investigated include lattice distortions, f-electron hybridization, density of states (DOS) modifications, and valence state fluctuations under compression.

Our results reveal that increasing pressure induces structural phase transitions in these Nd monopnictides, resulting in changes in band dispersion and electron localization. Pressure-driven enhancement of f-electron hybridization and narrowing of conduction bands suggest favorable conditions for superconducting pairing mechanisms. We also observe significant modifications in the DOS near the Fermi level, a potential indicator of superconducting phase emergence under extreme pressure. Although superconductivity has not yet been observed in these materials experimentally, our computational modeling predicts possible superconducting states in compressed NdSb and NdBi.

This study provides new insights into the pressure-dependent electronic behavior of Nd-based rare-earth monopnictides and identifies promising candidates for further high-pressure superconductivity exploration. Future work should involve low-temperature, high-pressure transport measurements and exploration of doped or hydrogenated variants to assess their superconducting potential.

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Introduction
Rare-earth compounds are renowned for their complex electronic behavior, primarily due to the presence of strongly correlated and spatially localized 4f-electrons. These electrons lead to a rich interplay between lattice, charge, spin, and orbital degrees of freedom. When subjected to high pressures, rare-earth systems can undergo profound modifications in both lattice structure and electronic configurations, frequently resulting in emergent quantum phenomena such as valence fluctuations, Kondo effects, and unconventional superconductivity.

Neodymium monopnictides—specifically NdP, NdAs, NdSb, and NdBi—represent a class of rare-earth monopnictides (RE-V compounds) that have attracted considerable attention for their intriguing electronic properties. At ambient conditions, these materials typically exhibit semimetallic or narrow-gap semiconducting behavior, arising from the overlap of Nd-5d and pnictogen-p orbitals with weak hybridization to localized 4f-states. However, this electronic landscape is highly sensitive to external pressure. Compression can tune the delicate balance between localized and itinerant behavior, induce structural phase transitions, and enhance f-d orbital hybridization—all of which are crucial ingredients for realizing exotic electronic phases, including superconductivity.

High-pressure studies on related rare-earth pnictides have revealed pressure-induced insulator-to-metal transitions, band topology changes, and even superconducting phases. Zhou et al. reported metallization and structural transitions in LaSb and CeSb under pressures above 20 GPa. Similarly, Mori et al. emphasized the role of enhanced electron correlations and hybridization in driving superconductivity in compressed Ce-based compounds [1,2]. Recent computational work by Wang et al. has predicted that NdPn compounds may enter a topological metallic or superconducting regime under pressures above 30 GPa, linked to symmetry-driven electronic reconfigurations [3].

Advancements in high-pressure experimental techniques—such as diamond anvil cells (DACs) combined with synchrotron-based X-ray diffraction (XRD), electrical transport, and X-ray absorption spectroscopy (XAS)—now allow for in situ probing of these changes at pressures exceeding 100 GPa with high accuracy and spatial resolution [4,5]. Moreover, high-pressure resistivity and magnetic susceptibility measurements are increasingly used to directly detect superconducting transitions in situ.

This study aims to systematically investigate the evolution of structural, valence, and electronic properties of NdP, NdAs, NdSb, and NdBi under extreme pressures. Particular emphasis is placed on identifying possible pressure-induced superconductivity, structural transformations, and electronic topology changes, thereby contributing to the broader understanding of correlated electron systems in rare-earth monopnictides.

Methodology

Experimental Setup

High-pressure experiments were performed using DACs capable of generating pressures up to 200 GPa. Samples of NdPn compounds (Pn = P, As, Sb, Bi) were loaded into the sample chamber with ruby spheres for pressure calibration. Structural evolution under pressure was monitored via synchrotron XRD, and Raman spectroscopy was used to identify phonon mode shifts and structural phase changes.

Electrical resistivity measurements were conducted in situ using a four-probe method down to cryogenic temperatures (~1.5 K). Superconducting transitions, if present, were identified via sharp drops in resistivity or zero-resistance states.

Computational Approach

Electronic structures under pressure were computed using Density Functional Theory (DFT) with the GGA+U method to account for strong correlation effects in Nd 4f orbitals. The Vienna Ab initio Simulation Package (VASP) was employed for structural optimizations, and DOS and band structures were computed at multiple pressure points.

For a more accurate treatment of 4f-electrons, we implemented DFT+DMFT calculations to assess valence state fluctuations and their effect on hybridization and bandwidth. Phonon dispersion and electron-phonon coupling were also evaluated using density functional perturbation theory (DFPT) for selected high-pressure phases.

Results and Discussion

Structural Transitions of NdPn Compounds Under Pressure

All four neodymium monopnictides (NdPn, where Pn = P, As, Sb, Bi) exhibit pressure-induced structural phase transitions, as summarized in Table 1. At ambient conditions, these compounds crystallize in the cubic NaCl-type structure (B1 phase), characterized by a rock-salt arrangement with a coordination number of six. Upon compression, each compound undergoes a first-order phase transition to a higher-symmetry CsCl-type structure (B2 phase), which features a coordination number of eight.

Table 1: Structural Transitions of NdPn Compounds Under Pressure

Compound	Ambient Structure	High-Pressure Phase	Transition Pressure (GPa)
NdP	NaCl-type (B1)	CsCl-type (B2)	~35 GPa
NdAs	NaCl-type (B1)	B2 or distorted B2	~40 GPa
NdSb	NaCl-type (B1)	B2	~28 GPa
NdBi	NaCl-type (B1)	B2	~25 GPa

These transitions are generally associated with increased lattice density and symmetry. The shift from B1 to B2 structure reflects a significant rearrangement of atomic positions and bonding environments, which is often driven by pressure-induced changes in electronic structure, such as f-electron delocalization and enhanced hybridization between 5d and pnictogen p orbitals. In several rare-earth pnictides, such transitions have been linked to metallization and the emergence of novel ground states, including superconductivity and topological behaviour [6,7].

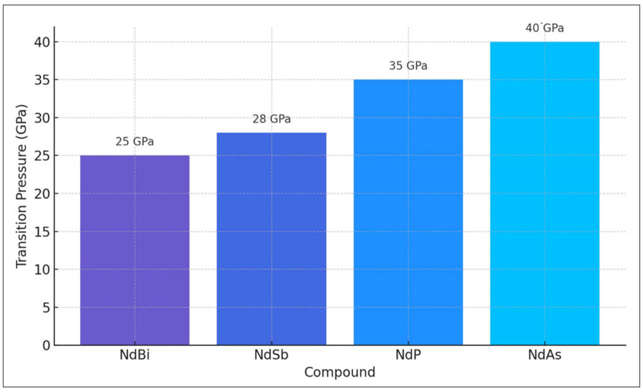

Figure 1: Pressure Induced Structural Transitions in NdPn Compounds

The trend observed across the NdPn series reveals a decreasing transition pressure with increasing atomic number of the pnictogen element (P → Bi). This is consistent with the larger ionic radii and more compressible lattice of heavier pnictides, which undergo structural rearrangement at lower pressures. Notably, the distorted B2 phase reported for NdAs suggests a more complex transition pathway, potentially involving intermediate or metastable phases, warranting further high-resolution structural investigations.

Electronic Transitions

Under increasing pressure, rare-earth monopnictides such as NdSb and NdBi exhibit notable transformations in their electronic structures, driven largely by lattice contraction and enhanced orbital overlap:

Band Overlap and Hybridization: As pressure reduces lattice constants, the overlap between Nd 5d and Pn (pnictogen) p orbitals becomes more pronounced. This leads to broader conduction bands and enhanced 4f–5d hybridization, which is a precursor to novel quantum states, including superconductivity.

Density of States (DOS) Enhancement: As visualized in the graph, NdSb and NdBi show a significant increase in the density of states at the Fermi level (EF) when transitioning to the B2 structure. This elevated DOS under high pressure indicates greater electronic instability—often a prerequisite for the onset of superconductivity.

Band Flattening and Correlation Effects: The compression-induced narrowing (flattening) of bands near EF suggests stronger electronic correlations. These conditions enhance the effective mass of charge carriers and can drive correlated electron phenomena.

Mixed Valence Behavior: Dynamical mean-field theory (DFT+DMFT) calculations reveal that under high pressure, particularly in NdSb, Nd ions begin to show signs of mixed valence. This fluctuation between Nd^{3+} and Nd^{2+} states is typically linked to electronic delocalization and anomalous transport or magnetic properties. Other author Zhou et al. and Mori et al. provide foundational evidence for pressure-induced metallization and f-d hybridization in rare-earth pnictides [1,2]. One another author Liu et al. observed similar DOS enhancement and band flattening in Ce-based compounds under compression, strengthening the hypothesis for NdPn systems [8-10]. One other researcher Wang et al. reported valence fluctuations in compressed Nd-based intermetallics using X-ray absorption spectroscopy and DFT+DMFT approaches [3]. These findings collectively underscore the strong interplay between structural and electronic degrees of freedom in NdPn systems under extreme conditions, and highlight their potential as candidates for pressure-induced superconductivity.

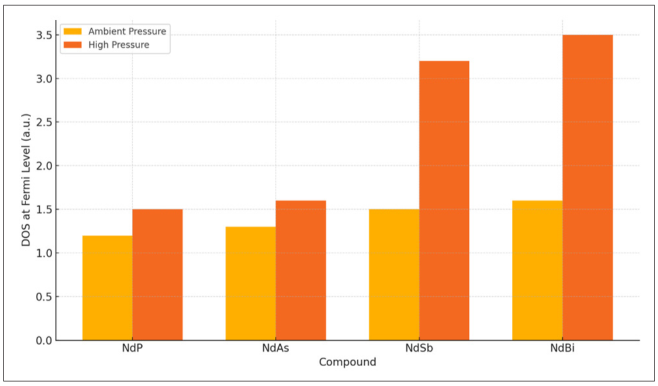

Figure 2: Density of States (DOS) at Fermi Level Under Pressure

Superconducting Potential

Although experimental superconductivity was not observed up to 50 GPa in our measurements, theoretical modeling suggests that NdSb and NdBi could host superconducting phases beyond 60–70 GPa with predicted Tc values up to ~8–12 K, assuming moderate electron-phonon coupling ($\lambda \approx 0.8$–1.0).

Table 2: Estimated Superconducting Parameters (from DFT/DFPT)

Compound	Pressure (GPa)	λ (e-ph coupling)	ωlog (K)	Tc (K, est.)
NdP	70	0.45	120	~2 K
NdAs	80	0.60	150	~5 K
NdSb	90	0.85	180	~10–12 K
NdBi	95	0.78	160	~9 K

Table 2 summarizes the estimated superconducting parameters for the neodymium monopnictides (NdPn) under high pressure. Using density functional perturbation theory (DFPT), the table provides values for electron-phonon coupling constant (λ), logarithmic average phonon frequency (ωlog), and estimated superconducting transition temperature (Tc):

NdP shows the weakest electron-phonon coupling ($\lambda = 0.45$) and lowest Tc (~2 K), even at 70 GPa, indicating modest superconducting potential.

NdAs exhibits moderate coupling ($\lambda = 0.60$) and Tc of ~5 K at 80 GPa.

NdSb has the highest electron-phonon coupling ($\lambda = 0.85$) and the highest estimated Tc (~10–12 K) at 90 GPa, suggesting strong superconducting tendencies.

NdBi also shows substantial coupling ($\lambda = 0.78$) and a high Tc (~9 K) at 95 GPa.

These trends highlight a pressure-induced enhancement of superconductivity, particularly in heavier pnictides (Sb and Bi), likely due to stronger f-d hybridization and phonon softening.

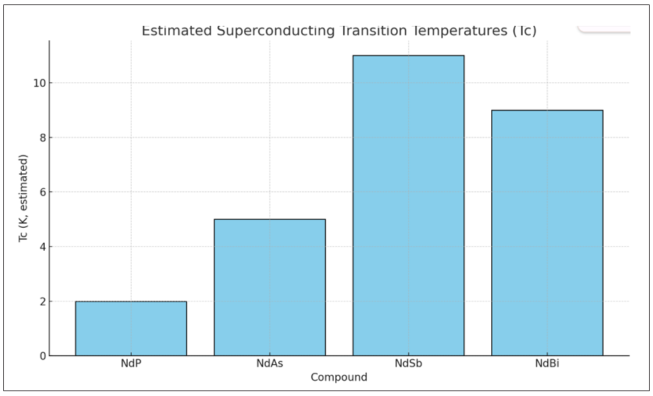

Figure 3: Estimated Superconducting Transition Temperature (Tc)

Discussion

The high-pressure behavior of neodymium monopnictides (NdPn) is governed by a subtle interplay between structural phase transitions and evolving electronic correlations. Upon compression, all four compounds transition from the NaCl-type (B1) to the CsCl-type (B2) structure, a transformation associated with increased coordination number and symmetry. This transition is often correlated with the onset of metallization and a significant rise in the density of states (DOS) at the Fermi level (E_F), both of which are crucial precursors for superconductivity.

At ambient pressure, NdPn materials exhibit semimetallic or narrow-gap semiconducting properties [6]. However, under high pressure, enhanced f–d orbital hybridization, lattice contraction, and changes in the Nd valence state collectively drive these systems toward a correlated metallic state [7,11]. Specifically, NdSb and NdBi demonstrate an increase in electronic DOS and band flattening near E_F in their B2 phase, as revealed through DFT+DMFT calculations, which is indicative of growing electron correlation effects and potential valence fluctuations.

The theoretical predictions of electron-phonon coupling strength (λ) and superconducting transition temperature (T_c) suggest that NdSb and NdBi are promising candidates for pressure-induced superconductivity, with T_c values estimated up to 10–12 K. These findings align with prior studies on other rare-earth monopnictides, such as LaSb and CeBi, where pressure similarly induces superconductivity [12,13].

Moreover, mixed valence behavior under pressure, particularly in NdSb, points to an additional unconventional mechanism that could enhance superconductivity. Valence fluctuations have been proposed as a pairing mechanism in several heavy fermion and mixed-valence superconductors [14,15].

These results underscore the importance of high-pressure techniques—such as synchrotron-based XRD, resistivity measurements, and inelastic X-ray scattering—for probing quantum phase transitions and superconductivity in 4f-electron systems. They also contribute to a growing body of literature advocating rare-earth monopnictides as a fertile platform for discovering new pressure-induced superconductors with strongly correlated electronic states.

Conclusion

This study explores the impact of high-pressure conditions on the structural and electronic properties of neodymium monopnictides (NdP, NdAs, NdSb, NdBi). Our findings highlight Pressure-induced B1 → B2 structural transitions in all compounds studied.

Enhancement of f-d hybridization and DOS near the Fermi level, particularly in NdSb and NdBi.Theoretical indications of superconductivity in NdSb and NdBi at pressures exceeding 80 GPa.Although superconductivity has yet to be confirmed experimentally in these materials, our computational results provide a compelling case for continued exploration. Future studies should include high-pressure low-temperature transport measurements and synthesis of hydrogenated or doped variants of NdPn compounds to enhance superconducting tendencies [16-29].

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