

Crystal field induced defect compensation in Gd-doped PbTiO₃ preserving ferroelectricity and *f*-electron magnetism together with finite-temperature multifunctionality

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Aliovalent rare-earth doping of ferroelectric oxides offers a route toward multifunctionality, yet its microscopic consequences remain poorly understood. Here we present a unified first-principles and crystal-field study of Gd³⁺-doped PbTiO₃, combining DFT + *U* and TB-mBJ electronic structure calculations with Wannier-based crystal-field extraction, superposition modeling, Berry-phase polarization, and finite-temperature statistical mechanics. We resolve a long-standing discrepancy between prior theoretical predictions of metallicity and experimental observations of insulating behavior by demonstrating that uncompensated Gd substitution is intrinsically unstable, whereas charge compensation via Pb or O vacancies restores finite band gaps and stabilizes the ferroic lattice. Two charge-neutral configurations, Pb_{0.8125}Gd_{0.125}TiO₃ and PbTi_{0.875}Gd_{0.125}O_{2.9375}, are shown to be thermodynamically stable, exhibiting near-pristine spontaneous polarizations ($|\Delta P| \approx 82\text{--}84\text{ }\mu\text{C}/\text{cm}^2$) and robust localized $4f^7$ moments ($\sim 7\mu_B$). Symmetry analysis clarifies why macroscopic ferroelectricity survives strong local site symmetry breaking: the global $\Gamma_{15} \rightarrow A_1$ polar mode remains symmetry-allowed, while defects primarily modulate local distortion amplitudes. Crystal-field theory reveals pronounced single-ion anisotropy induced by vacancy-driven symmetry reduction, whereas intersite exchange remains ultraweak ($J \sim 10^{-3}\text{ meV}$) due to the spherical $4f^7$ configuration and unfavorable superexchange geometry, precluding magnetic order at accessible temperatures. Thermal disorder of the Gd moments is shown to induce an exchange-driven optical-gap redshift of $\sim 0.2\text{--}0.4\text{ eV}$, linking magnetism and optics without compromising ferroelectricity. These results establish charge compensation as the organizing principle governing structure, ferroic order, and electronic response in rare-earth-doped PbTiO₃, and provide a transferable framework for defect-engineered multifunctional perovskites beyond conventional multiferroic paradigms.

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I. INTRODUCTION

Lead titanate (PbTiO₃, PTO) is a prototypical displacive ferroelectric oxide with a high Curie temperature ($T_{\text{FE}} \approx 763\text{ K}$) and a large spontaneous polarization, making it a benchmark system for understanding polarization mechanisms and a technologically relevant material for high-temperature dielectric and piezoelectric applications [1]. Upon cooling from the cubic paraelectric phase, PTO undergoes a symmetry-breaking transition to a tetragonal ferroelectric structure driven by the unstable Γ_{15} polar soft mode, accompanied by a pronounced tetragonality ($c/a \approx 1.064$) that underpins its functional properties [2]. At the same time, this strong distortion generates internal stresses during processing, motivating extensive efforts to tailor PTO through chemical substitution and defect engineering [3–6].

Aliovalent rare-earth (RE) substitution has emerged as a particularly effective strategy. Substitution of Pb²⁺ or Ti⁴⁺ by trivalent RE ions can improve sinterability, densification,

and dielectric performance, while simultaneously introducing local defect dipoles and strain fields that modify electromechanical coupling [7,8]. Among RE dopants, Gd³⁺ is of special interest: its half filled $4f^7$ shell carries a large, nearly atomic magnetic moment; its ionic radius is comparable to Pb²⁺; and its aliovalent charge necessitates intrinsic compensation mechanisms that directly couple lattice, charge, and electronic degrees of freedom. Experimentally, Gd-modified Pb-based perovskites exhibit enhanced dielectric and piezoelectric responses [9], while reports of magnetic signatures under specific conditions have raised the broader question of how localized *f* moments coexist with ferroelectric order [10].

From a fundamental perspective, this coexistence poses two intertwined challenges. First, introducing magnetism into a ferroelectric does *not* automatically yield a useful multiferroic material: strong magnetoelectric coupling typically requires specific symmetry conditions or exchange mechanisms that are absent in most oxide perovskites. Second, aliovalent substitution profoundly perturbs the electronic structure, and early first-principles studies of Gd-doped PTO predicted metallic behavior—at odds with experiments that consistently report insulating samples [10–12]. Resolving this discrepancy is essential not only for materials design, but also

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for establishing a physically consistent description of defect-controlled ferroelectrics.

Our earlier work [13] demonstrated that Pb-site substitution by Gd^{3+} is energetically favored in PTO, but also revealed that uncompensated aliovalent doping drives spurious band-gap closure. This result highlighted a missing element common to many prior theoretical treatments: intrinsic charge compensation. In real materials, Gd substitution is inevitably accompanied by compensating vacancies or defects, which fundamentally alter the electronic ground state, local symmetry, and magnetic response.

In this work, we show that charge compensation is the organizing principle governing the ferroic, magnetic, and optoelectronic behavior of Gd-doped PbTiO_3 . We systematically investigate two physically motivated, charge-neutral configurations: (i) $\text{Pb}_{0.8125}\text{Gd}_{0.125}\text{TiO}_3$ stabilized by a Pb vacancy, and (ii) $\text{PbTi}_{0.875}\text{Gd}_{0.125}\text{O}_{2.9375}$ stabilized by an oxygen vacancy. Using a coordinated framework that combines density-functional theory with on-site correlations, Wannier-based crystal-field analysis, semiempirical superposition modeling, Berry-phase polarization theory, and finite-temperature statistical mechanics, we demonstrate that both configurations are thermodynamically stable, insulating, and ferroelectrically robust.

A major conceptual distinction emphasized throughout this work is that between *global* crystal symmetry and the *local site symmetry* of individual ions, defined by their point-symmetry groups in the presence of defects. Macroscopic ferroelectricity in PTO is governed by the global space-group symmetry: as long as the tetragonal $P4mm$ structure permits the $\Gamma_{15} \rightarrow A_1$ polar distortion, a nonzero polarization remains symmetry-allowed. Local symmetry breaking induced by Gd substitution and nearby vacancies modifies the *amplitude* and local environment of polar displacements but does not eliminate the global polar order parameter. Conversely, magnetic and crystal-field properties are controlled by the *local site symmetry* of individual Gd ions, given by the corresponding point-symmetry groups. Although dopants and vacancies are expected to be distributed in a largely disordered manner in real samples, each vacancy-associated Gd center retains a locally reduced symmetry that governs its crystal-field and magnetic response, while macroscopic observables reflect orientational and configurational averaging rather than restoration of higher local symmetry.

Within this framework, we show that robust ferroelectric polarization ($|\Delta P| \approx 82\text{--}84 \mu\text{C}/\text{cm}^2$) coexists with strong but localized $4f^7$ moments ($\sim 7\mu_B$), while long-range magnetic order is suppressed by symmetry and geometry. The nearly spherical $4f^7$ charge distribution of Gd^{3+} , unfavorable superexchange pathways in the perovskite lattice, and the dominance of single-ion crystal-field anisotropy and level splittings collectively yield ultraweak intersite exchange interactions ($J \sim 10^{-3} \text{ meV}$). As a result, the system is strictly multiferroic only below a vanishingly small magnetic ordering temperature, while at experimentally relevant temperatures it realizes a *multifunctional* regime in which robust ferroelectricity coexists with paramagnetic f moments and tunable electronic and optical properties.

By resolving the long-standing metallicity paradox and establishing charge compensation as the unifying microscopic

mechanism, this work goes beyond reconciling theory with experiment. It provides a predictive, symmetry-consistent framework for understanding how defects, local symmetry, and electronic correlations jointly control polarization, magnetism, and band structure in rare-earth-doped perovskites. The insights developed here are broadly applicable to defect-engineered ferroelectrics and multifunctional oxides, where local symmetry breaking can be harnessed to tune magnetic and optical responses without compromising macroscopic ferroelectric order.

II. RESULTS AND DISCUSSION

Building on our preceding work [13] identifying Gd^{3+} site preference in PbTiO_3 , this study addresses the remaining challenge: the metallic behavior of charge-uncompensated systems. We show that intrinsic defect compensation—via Pb or O vacancies—is essential to recover the insulating ground state and stabilize ferroic functionality.

We construct several charge-neutral configurations representative of realistic local dopant environments and assess their structural, electronic, magnetic, and ferroelectric properties. This study elucidates how defect-dopant interactions mediate the interrelationships between ferroelectricity and magnetism. While long-range magnetic order appears only below T_C^{MF} (Table VI), the coexistence of ferroelectricity and paramagnetism at room temperature renders these systems multifunctional.

The subsequent sections detail the results of our multifaceted considerations, including: structural models (Sec. II A), lattice properties (Sec. II B), electronic structure (Secs. II C 1 and II C 2), electronic and optical band gaps (Sec. II C 3), magnetic properties (Sec. II C 4), formation energies (Sec. II D), charge redistribution (Sec. II E), magnetic response from crystal field theory (CFT) (Sec. II F), CF-controlled magnetism and finite-temperature optical redshift (Sec. II G), polarization behavior (Sec. II H), and global symmetry-preserved polarization and local symmetry-tuned magnetism (subsection of Sec. II H). These considerations offer a framework for predicting and engineering tunable multiferroic and multifunctional properties in rare-earth-doped PbTiO_3 through intrinsic defect modulation.

A. Defect-design structural models of Gd^{3+} doping in ferroelectric PbTiO_3

Figure 1 illustrates the defect-designed Gd-doped PbTiO_3 structures studied to explore aliovalent doping effects in the tetragonal phase (C_{4v}^1 , $P4mm$) [14]. We simulate charge-uncompensated and charge-neutral systems using $2 \times 2 \times 2$ and $2 \times 2 \times 4$ supercells, respectively.

Figure 1(a) shows $\text{Pb}_{0.875}\text{Gd}_{0.125}\text{TiO}_3$ structure, where Gd^{3+} substitutes Pb^{2+} without charge compensation. Although structurally simple, this leads to metallic behavior with the Fermi level intersecting the conduction band [Fig. 2(b), Fig. 3(c)], contradicting optical and transport experiments that report insulating Gd-doped PbTiO_3 [15].

Figures 1(b) and 1(c) depict charge-compensated configurations that recover insulating behavior. In Fig. 1(b), a Pb-site vacancy (V_{Pb}) compensates excess positive charge from Gd^{3+} , forming $\text{Pb}_{0.8125}\text{Gd}_{0.125}\text{TiO}_3$. This is typical of

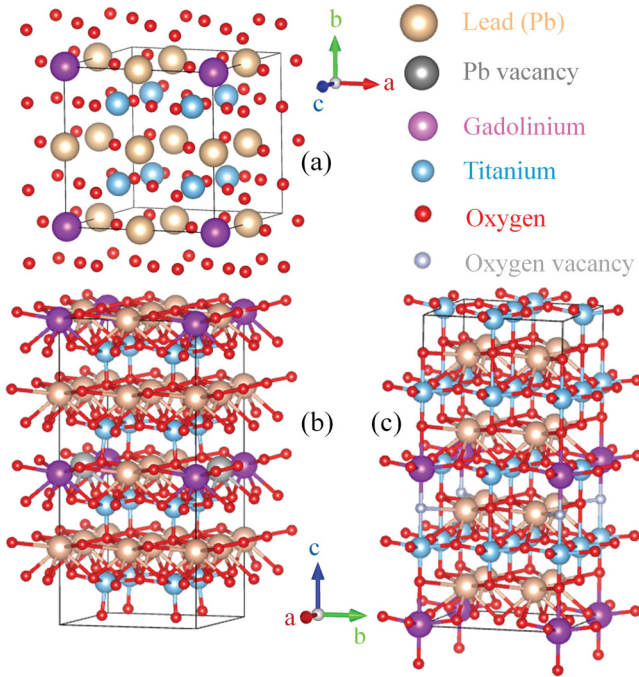


FIG. 1. Optimized supercells of (a) $\text{Pb}_{0.875}\text{Gd}_{0.125}\text{TiO}_3$ (Gd on Pb site, uncompensated), (b) $\text{Pb}_{0.8125}\text{Gd}_{0.125}\text{TiO}_3$ (Gd on Pb site with a Pb vacancy), and (c) $\text{PbTi}_{0.875}\text{Gd}_{0.125}\text{O}_{2.9375}$ (Gd on Ti site with an O vacancy), modeled in $2 \times 2 \times 2$ and $2 \times 2 \times 4$ supercells, respectively. Here, $x = 1/8 = 0.125$ denotes the Gd content, and $\delta = 1/16 \approx 0.0625$ represents the vacancy concentration.

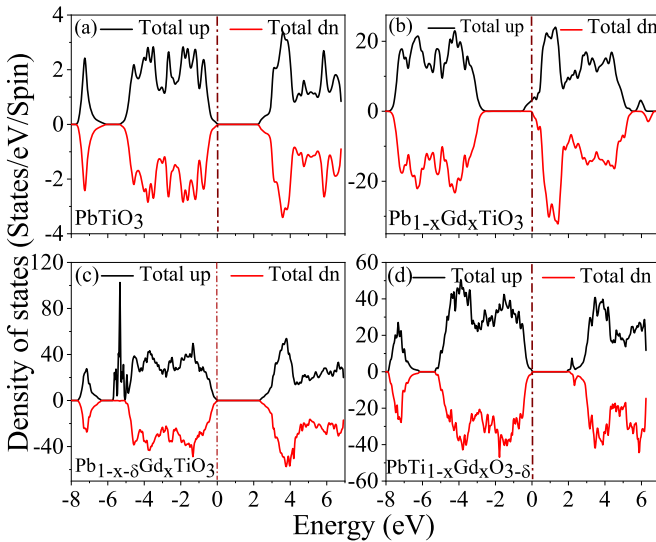


FIG. 2. Spin-polarized total density of states (DOS) calculated within GGA + U for (a) pristine PbTiO_3 , (b) $\text{Pb}_{1-x}\text{Gd}_x\text{TiO}_3$ (uncompensated Pb-site Gd substitution), (c) $\text{Pb}_{1-x-\delta}\text{Gd}_x\text{TiO}_3$ (Pb-site Gd with Pb vacancy), and (d) $\text{PbTi}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$ (Ti-site Gd with O vacancy). The Fermi level is set to 0 eV (vertical dashed line). Uncompensated Gd substitution introduces Gd 4*f* states at E_F , driving metallicity, whereas intrinsic vacancies restore an insulating gap and preserve strong spin asymmetry.

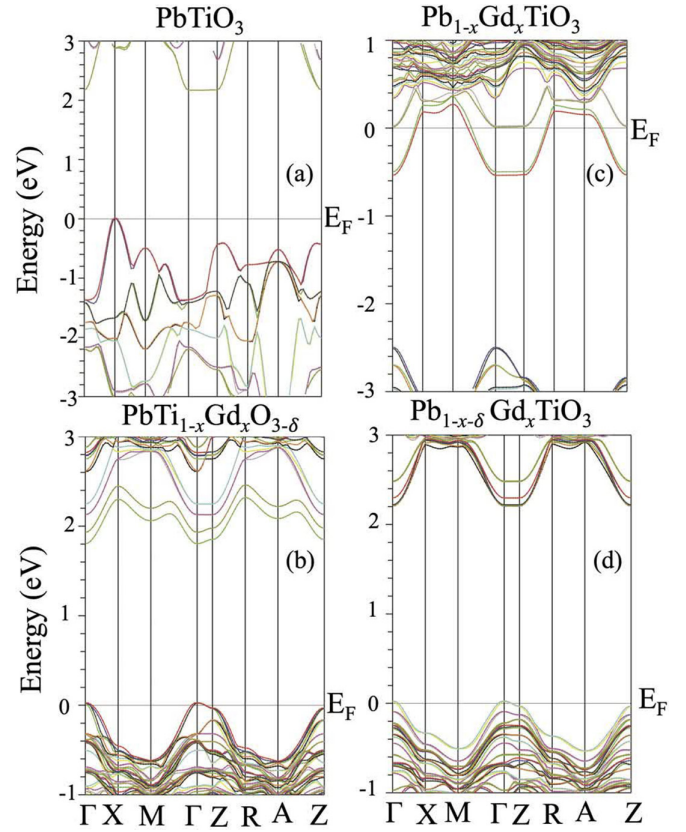


FIG. 3. Spin-polarized PBE-GGA + U electronic band structures for (a) pristine PbTiO_3 , (b) $\text{PbTi}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$ with Ti-site Gd^{3+} and V_O , (c) $\text{Pb}_{1-x}\text{Gd}_x\text{TiO}_3$ with uncompensated Pb-site Gd, and (d) $\text{Pb}_{1-x-\delta}\text{Gd}_x\text{TiO}_3$ with V_Pb ($x = 1/8$, $\delta = 1/16$). Only spin-up bands are shown for clarity, as spin asymmetry is minimal. The Fermi level is set to 0 eV.

A-site donor doping mechanisms in perovskites, yielding a locally distorted but energetically stable lattice with a semi-conducting band gap.

Figure 1(c) shows the B-site doped system $\text{PbTi}_{0.875}\text{Gd}_{0.125}\text{O}_{2.9375}$, where Gd^{3+} replaces Ti^{4+} and is compensated by an O vacancy (V_O). Although less common experimentally, this configuration allows investigation of distinct local site symmetry, CFs, and potential 4*f*–3*d* hybridization, relevant for magnetoelectric coupling.

Together, these three defect-designed models span the key doping and compensation scenarios relevant to Gd-doped PbTiO_3 films and ceramics. They form the atomistic foundation for understanding the interrelationships between defect configuration and ferroic behavior, and provide structural blueprints for realizing multiferroic and magnetoelectric functionalities, with relevance for synthesis, diffraction, and local magnetic characterization.

B. Defect-stabilized lattice and elastic properties in Gd-doped PbTiO_3

Table I presents the optimized lattice parameters, tetragonality, and elastic constants for vacancy-compensated Gd-doped PbTiO_3 . Both FM and AFM configurations were examined, yielding nearly identical results, underscoring that

TABLE I. Lattice parameters a , c (Å), tetragonality c/a , bulk modulus B (GPa), and pressure derivative B' for Gd-doped PbTiO_3 with intrinsic vacancies, compared with pristine PbTiO_3 . Configurations include $\text{Pb}_{0.8125}\text{Gd}_{0.125}\text{TiO}_3$ (Pb vacancy V_{Pb}) and $\text{PbTi}_{0.875}\text{Gd}_{0.125}\text{O}_{2.9375}$ (O vacancy V_{O}) at $x = 0.125$, $\delta \approx 0.0625$. Both FM and AFM orderings are considered. Unit-cell values are obtained by scaling relaxed supercell dimensions for direct comparison with pristine PbTiO_3 .

Compound	Vacancy	Phase	Scheme	Unit Cell			Supercell			Elastic Properties	
				a (Å)	c (Å)	c/a	a (Å)	c (Å)	c/a	B (GPa)	B'
$\text{Pb}_{1-x-\delta}\text{Gd}_x\text{TiO}_3$	V_{Pb}	FM	PBE-GGA + U	3.911	4.137	1.058	7.823	16.550	2.116	167.696	4.209
$\text{Pb}_{1-x-\delta}\text{Gd}_x\text{TiO}_3$	V_{Pb}	AFM	PBE-GGA + U	3.911	4.137	1.058	7.823	16.550	2.116	167.694	4.208
$\text{PbTi}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$	V_{O}	FM	PBE-GGA + U	3.989	4.211	1.055	7.978	16.844	2.111	152.287	4.571
$\text{PbTi}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$	V_{O}	AFM	PBE-GGA + U	3.989	4.211	1.055	7.978	16.844	2.111	152.287	4.571
PbTiO_3 [13]	None	NM	PBE-GGA	3.933	4.191	1.066				160.351	4.49

magnetism has negligible impact on the equilibrium lattice geometry.

Relative to pristine PbTiO_3 [13], Pb-site doping with V_{Pb} slightly contracts the lattice but preserves tetragonality ($c/a \approx 1.058$), consistent with stable incorporation of the defect complex. In contrast, Ti-site doping with V_{O} expands both a and c , reducing c/a to ~ 1.055 . Thus, the unit cell volume decreases for A-site substitution and increases for B-site substitution, reflecting stronger bonding in the $\text{Pb} - \text{Gd} - V_{\text{Pb}}$ case and weaker bonding in the $\text{Ti} - \text{Gd} - V_{\text{O}}$ case. These contrasting trends will be further analyzed in Sec. II E via charge density and bonding analysis.

Bulk moduli also follow opposite tendencies: $\text{Pb}_{0.8125}\text{Gd}_{0.125}\text{TiO}_3$ is stiffer ($B \sim 168$ GPa) than pristine PbTiO_3 ($B \sim 160$ GPa), whereas $\text{PbTi}_{0.875}\text{Gd}_{0.125}\text{O}_{2.9375}$ is softer ($B \sim 152$ GPa). Because B and B' are sensitive to fitting interval, these comparisons should be treated qualitatively, yet they clearly indicate how vacancy location governs the elastic response.

Overall, both defect-stabilized models maintain the tetragonal perovskite structure at realistic doping levels ($x = 0.125$, $\delta \approx 0.0625$), confirming that intrinsic vacancies allow stable incorporation of aliovalent Gd. The opposite lattice and elastic responses between A-site and B-site substitutions provide atomistic evidence of how charge compensation routes directly control bonding strength and mechanical resilience in Gd-modified PbTiO_3 .

C. Electronic structures

1. Density of states in Gd-doped PbTiO_3

Figure 2 highlights the essential electronic mechanisms induced by Gd substitution and intrinsic defect compensation in PbTiO_3 within GGA + U . The total density of states (DOS) directly reveals how aliovalent doping and vacancy formation govern the competition between metallicity, insulation, and spin polarization.

Pristine PbTiO_3 [Fig. 2(a)] shows a well-defined insulating gap with symmetric spin channels, consistent with its nonmagnetic ferroelectric ground state. In contrast, uncompensated Pb-site Gd substitution [Fig. 2(b)] introduces narrow, strongly spin-polarized Gd 4*f* states at the Fermi level E_F , driving a metallic state and demonstrating that charge imbalance cannot be accommodated without defects.

Charge compensation via intrinsic vacancies restores insulating behavior. In $\text{Pb}_{1-x-\delta}\text{Gd}_x\text{TiO}_3$ [Fig. 2(c)], Pb vacancies

shift the Gd 4*f* states away from E_F , reopen the band gap, and preserve pronounced spin asymmetry. A comparable stabilization occurs for Ti-site Gd substitution with O vacancies [Fig. 2(d)], confirming that vacancy-assisted charge compensation is a robust route to insulating, spin-polarized states.

Overall, Fig. 2 establishes the main electronic result of this work: uncompensated Gd doping destabilizes the insulating state, whereas intrinsic vacancies recover an insulating gap while retaining localized magnetic moments. The orbital-resolved origin of these trends is provided in the Supplemental Material (SM) (Fig. SM2 in Ref. [16]). Additional computational details, extended derivations, Supplemental figures and tables, and supporting analyses underlying the results presented here are provided in the SM (see also Refs. [10,13,15,17–88] therein).

2. Band structure

Figure 3 complements the DOS analysis (Fig. 2), providing momentum-resolved insight into how Gd doping and vacancy compensation affect the electronic spectrum. Together with Table II and polarization results (Fig. 6), these band structures form the backbone of the proposed multiferroicity design strategy.

Pristine PbTiO_3 [Fig. 3(a)] shows a well-defined indirect gap ($E_g \sim 2.20$ eV), with dispersive Ti 3*d* conduction bands and flatter O 2*p* valence bands. This electronic structure underpins its ferroelectric semiconducting behavior and validates the Berry phase formalism for polarization (Sec. II H).

Uncompensated Pb-site doping [Fig. 3(c)] collapses the gap: flat Gd 4*f* bands cross E_F , producing metallicity and invalidating ferroelectric polarization. This scenario contradicts experimental studies reporting semiconducting Gd-doped PbTiO_3 [10], thus confirming that vacancies are essential for a realistic description of properties of $\text{PbTiO}_3\text{:Gd}^{3+}$.

Charge-compensated models reveal restoring of semiconducting properties. With V_{Pb} [Fig. 3(d)], the gap reopens to ~ 2.23 eV, while Ti-site doping with V_{O} [Fig. 3(b)] yields a smaller gap of ~ 1.84 eV. Both models retain polarization values close to that observed for pristine PbTiO_3 (-83 to -84 $\mu\text{C}/\text{cm}^2$, Fig. 6). Notably, compensated systems exhibit flatter conduction bands than pristine PbTiO_3 , signaling increased localization from Gd 4*f* – Ti 3*d* hybridization. While reduced dispersion may diminish carrier mobility, it stabilizes the off-centered Ti displacements that are essential to ferroelectricity.

TABLE II. Crystal phase, exchange-correlation (XC) scheme, U_{eff} for Ti and Gd, spin-orbit coupling (SOC), and electronic band gaps E_g^e (type), along with direct and indirect optical onsets $E_{g,\text{dir}}^{\text{opt}}$ and $E_{g,\text{ind}}^{\text{opt}}$. Systems include pristine PbTiO_3 , $\text{Pb}_{0.8125}\text{Gd}_{0.125}\text{TiO}_3$ with a Pb vacancy, and $\text{PbTi}_{0.875}\text{Gd}_{0.125}\text{O}_{2.9375}$ with an O vacancy, using $x = 0.125$ and $\delta = 0.0625$. Values marked * are from this work; others are taken from the literature.

Compound	Form	Structure	Phase	Scheme	SOC	c	$U_{\text{eff}}^{\text{Ti}}$	$U_{\text{eff}}^{\text{Gd}}$	E_g^e	Type	$E_{g,\text{dir.}}^{\text{opt}}$	$E_{g,\text{ind.}}^{\text{opt}}$	Ref.					
Pb _{1-x} Gd _x TiO ₃	Bulk	Tetragonal	FM	PBE-GGA + U	Yes				4.35	0.00	0.0	0.0	*					
Pb _{1-x-δ} Gd _x TiO ₃												4.35	1.82	dir.	3.5	2.5	*	
												3.94	4.35	2.23		3.7	2.8	*
PbTi _{1-x} Gd _x O _{3-δ}												4.35	1.73		3.4	2.6	*	
							3.94	4.35	1.84		3.7	2.6	*					
PbTiO ₃			NM	PBE-GGA					1.78	ind.	3.2	2.5	*					
				PBE-GGA + U	3.94		2.20		3.5	2.6	*							
				TB-mBJ	1.38		2.08		3.6	3.1	*							
				JTSKTB-mBJ	1.80		2.60		3.7	3.2	*							
		Cubic		PW91-GGA	No				1.56	dir.			[75]					
			B3PW					2.87	[76]									
	Thin Films	Tetragonal		Exp.							3.45		[77]					
										3.7		[78]						
											3.88		[79]					
		Cubic									3.67		[79]					
	Nanoparticle	Tetragonal										2.6	[80]					

These features linked directly to the orbital contributions discussed in Sec. SM III in Ref. [16]. Pb lone-pair activity, evident from the Pb 6s DOS peak (Fig. SM2(a₂) in Ref. [16]), diminishes upon Gd substitution, thus weakening Pb-driven ferroelectricity. Simultaneously, Ti–O hybridization strengthens (Figs. SM2(d₃) and SM2(c₃) in Ref. [16]), consistent with narrower conduction bands, see, Figs. 3(b) and 3(d). Thus, ferroelectricity is preserved not by Pb lone pairs but by enhanced Ti–O ionicity.

Methodologically, GGA + U mitigates self-interaction errors in localized Ti 3d and Gd 4f states, improving their orbital localization, spin polarization, and the stability of insulating solutions compared to semilocal GGA approaches [89,90]. Without U , PbTiO_3 band gaps are underestimated and Gd f states spuriously delocalize, leading to false metallicity. Hybrid TB-mBJ and JTSKTB-mBJ functionals [48,49,54] improve optical gaps but do not preserve the correct local spin alignment or exchange splitting, making spin-polarized GGA + U the optimal choice for exploring multiferroicity.

In short, the band structures reveal the distinct yet complementary roles of Gd doping and intrinsic defects: uncompensated Gd substitution drives metallicity and suppresses ferroelectric order, whereas defect compensation through Pb or O vacancies reopens the band gap, stabilizes polarization along the polar c axis, and enables localized magnetic moments. This cooperative interaction between Gd-derived flat bands and vacancy-induced semiconductivity substantiates the design principle that multiferroicity in PbTiO_3 arises from coupled charge, spin, and orbital degrees of freedom.

3. Electronic and optical band gaps

The perpendicular extinction coefficient $k_{\perp}(\omega)$, obtained within the independent-particle RPA, was converted to the absorption coefficient as $\alpha(\omega) = \frac{2\omega}{c} k_{\perp}(\omega) = \frac{4\pi}{\lambda} k_{\perp}(\omega)$, and

the Tauc relation:

$$(\alpha E)^{\gamma} = B(E - E_g^{\text{opt}}), \quad \gamma = \begin{cases} 2 & \text{direct-allowed,} \\ 1/2 & \text{indirect-allowed,} \end{cases} \quad (1)$$

was applied to extract linear regimes and optical onsets (Fig. 4). The use of $k_{\perp}(\omega)$ is preferred in tetragonal PbTiO_3 because $k_{\parallel}(\omega)$ systematically overestimates gaps due to stronger dielectric screening along the polar axis.

For pristine PbTiO_3 , JTSKTB-mBJ functional with $c = 1.80$ yields $E_{g,\text{dir}}^{\text{opt}} \approx 3.7$ eV and $E_{g,\text{ind}}^{\text{opt}} \approx 3.2$ eV, while TB-mBJ functional with $c = 1.38$ gives 3.6 and 3.1 eV, respectively. These values track the experimental thin-film interval of 3.45–3.88 eV [78,79]. By contrast, PBE-GGA underestimates both edges, and PBE-GGA + U raises the direct onset to about 3.5 eV but leaves the indirect onset near 2.6 eV. Nanoparticle experiments show lower indirect gaps near 2.6 eV [80], consistent with finite-size and disorder effects, and with thermal redshift of the onset discussed in Sec. II G. Together, these comparisons indicate that the mBJ family is most reliable for quantitative optical benchmarking, whereas PBE-GGA + U provides the most balanced description of electronic gaps, magnetic moments, and d/f localization (Secs. II C 1 and II C 2).

In doped systems, the optical band gap trends observable in Table II and Fig. 4 clearly confirm that charge compensation is the decisive microscopic mechanism controlling the preservation of insulating character and the modifying of the optical and electronic gaps. Uncompensated Pb-site Gd yields metallic $\text{Pb}_{1-x}\text{Gd}_x\text{TiO}_3$ with $E_g^e = 0$, consistent with Gd-4f bands crossing the Fermi level (Secs. II C 1 and II C 2). Introducing intrinsic vacancies restores semiconductivity: for $\text{Pb}_{0.8125}\text{Gd}_{0.125}\text{TiO}_3$ with V_{Pb} , E_g^e ranges from 1.82 eV (without $U_{\text{eff}}^{\text{Ti}}$) to 2.23 eV (with $U_{\text{eff}}^{\text{Ti}} = 3.94$ eV), with direct optical onsets of 3.5–3.7 eV and indirect onsets of 2.5–2.8 eV. For

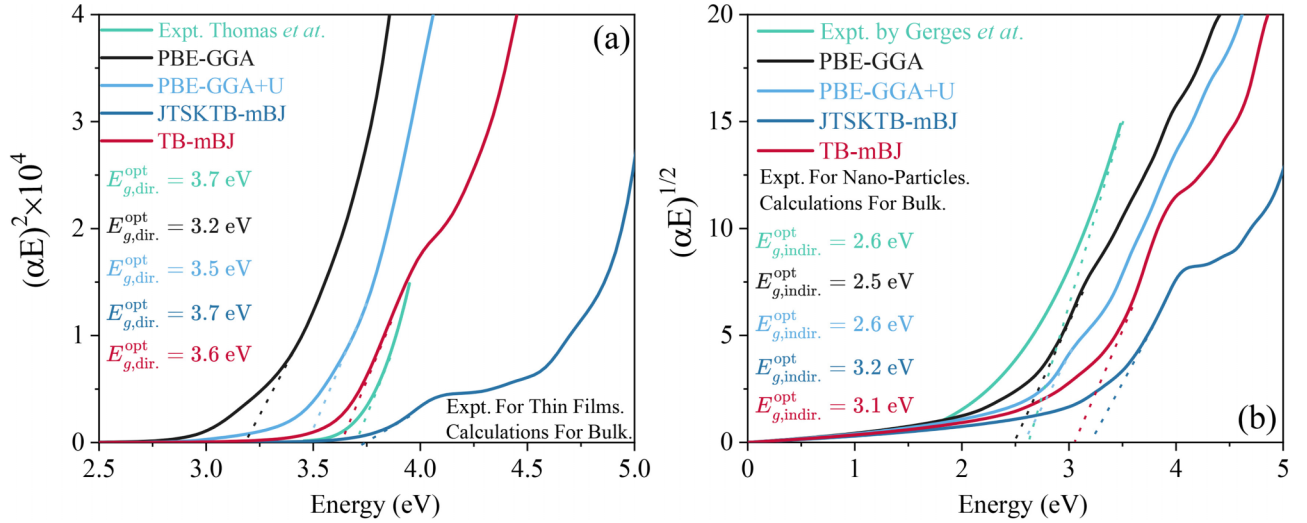


FIG. 4. Tauc analysis of optical band gaps in PbTiO₃: (a) direct $(\alpha E)^2$ vs E and (b) indirect $(\alpha E)^{1/2}$ vs E , constructed from RPA extinction spectra using PBE-GGA, PBE-GGA + U , TB-mBJ, and JTSKTB-mBJ. Linear fits yield $E_{g,dir}^{opt}$ and $E_{g,ind}^{opt}$. Experimental data for thin films [78] and nanoparticles [80] are shown for comparison.

PbTi_{0.875}Gd_{0.125}O_{2.9375} with V_O , E_g^e lies between 1.73 and 1.84 eV, with optical edges of 3.4–3.7 eV (direct) and about 2.6 eV (indirect). In both cases, vacancies shift the Gd-derived f states away from E_F , increase Ti–O ionicity, and modestly flatten the conduction bands, thereby reconciling semiconductivity with the persistence of local Gd moments and large Berry phase polarizations (Secs. II E, II H).

Although some compensated structures exhibit direct electronic gaps of 1.8–2.2 eV, the first robust optical edges extracted from Eq. (1) remain near 3.5–3.7 eV. This separation reflects the distinction between electronic thresholds and dipole-allowed transitions. In practice, mBJ functionals (especially JTSKTB-mBJ) provide quantitative optical gaps, while spin-polarized PBE-GGA + U with $U_{eff}^{Ti} = 3.94$ eV and $U_{eff}^{Gd} = 4.35$ eV captures d/f localization, magnetic order, and CF splittings relevant for magnetism and polarization (Secs. II F, II G).

Overall, the band-gap analysis reveals that aliovalent Gd doping requires intrinsic defect compensation to maintain an insulating ground state. The resulting compensated systems exhibit direct optical edges in the 3.5–3.7 eV range and indirect edges between 2.5 and 3.2 eV, placing both pristine and doped PbTiO₃ in the near-UV. This electronic structure is consistent with that encountered in ferroelectric photovoltaics and UV photodetectors, where large polarization coexists with a direct optical gap, and provides a coherent framework for integrating spectroscopy, magnetism, and polarization in the defect-driven multiferroic design.

4. Magnetic moments of Gd³⁺ in pristine and doped PbTiO₃

The spin decomposition in Table III reconciles DFT results with the atomic $4f^7$ configuration of Gd³⁺, which with $S = 7/2$ and $L = 0$ yields a spin-only saturation of $7.0 \mu_B$. Muffin-tin values lie between 6.8 and $6.9 \mu_B$, reduced slightly by hybridization with O $2p$ and Ti $3d$ states. Once the interstitial polarization is consistently partitioned (for 1-Gd cells $MM_{spin}^{Gd_1} = MM_{MT}^{Gd_1} + MM_{int}$, for 2-Gd cells

$MM_{spin}^{Gd_i} = MM_{MT}^{Gd_i} + \frac{1}{2} MM_{int}$, and per-site totals $MM_{tot}^{Gd_i} = MM_{spin}^{Gd_i} + MM_{orb}^{Gd_i}$), the effective per-site spins converge to $6.9 \mu_B - 7.3 \mu_B$, while orbital contributions are negligible ($\leq 0.02 \mu_B$), confirming complete quenching of the orbital momentum L . The uncompensated Pb_{1-x}Gd_xTiO₃ shows a larger interstitial contribution ($\sim 0.40 \mu_B$), inflating the apparent moment, but compensated supercells redistribute this polarization evenly, yielding values essentially indistinguishable from the atomic limit. Quantitatively, the deviation from $7.0 \mu_B$ is captured by $RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (M_i - 7.0)^2}$, which drops from $\sim 2.6 \mu_B$ in the uncompensated case to below $0.1 \mu_B$ once vacancies are introduced, providing clear evidence that charge compensation restores robust high-spin moments.

The total magnetic moments MM_{tot} in Table III of $7.95 \mu_B$, $13.91 \mu_B$, and $13.91 \mu_B$ demonstrate additivity and confirm that the determined moments are not finite-size artifacts. Residual contributions from Pb, Ti, and O are weak and antipolarized, consistent with the exchange-induced asymmetries seen in the DOS (Sec. II C 1). The negligible orbital contribution of the half filled $4f^7$ configuration leads to nearly isotropic $\mathbf{g} \simeq 2$ behavior, consistent with EPR measurements of Gd³⁺ complexes in oxides and frozen solutions, where the Zeeman interaction is essentially isotropic and dominated by spin-only character [91]. Consequently, both the $\mathbf{g}$ - and magnetic-susceptibility tensors are nearly isotropic. Consequently, the magnetocrystalline anisotropy energy is minimal—an advantageous trait for multiferroics, where large spin moments can coexist with switchable ferroelectric polarization without competing domain pinning.

These results reveal that Gd³⁺ retains an essentially atomic $4f^7$ high-spin state in the polar PbTiO₃ lattice. The interstitial polarization provides a sensitive fingerprint of compensation chemistry but does not alter the magnitude of the local moment. This robustness is key to the multifunctional response: strong local spins are preserved while electronic and structural degrees of freedom accommodate defect-driven charge balance. At finite temperature, exchange interactions and spin

TABLE III. Spin-polarized DFT results for muffin-tin spin $MM_{MT}^{Gd_i}$, orbital moment $MM_{orb}^{Gd_i}$, and interstitial polarization MM_{int} . Per-site spin moments are defined as $MM_{spin}^{Gd_i} = MM_{MT}^{Gd_i} + MM_{int}$ for single-Gd supercells, and $MM_{spin}^{Gd_i} = MM_{MT}^{Gd_i} + \frac{1}{2}MM_{int}$ when two Gd ions are present. The total per-site value is $MM_{tot}^{Gd_i} = MM_{spin}^{Gd_i} + MM_{orb}^{Gd_i}$. All values in μ_B .

Compound	Supercell	$MM_{MT}^{Gd_1}$	$MM_{spin}^{Gd_1}$	$MM_{orb}^{Gd_1}$	$MM_{MT}^{Gd_2}$	$MM_{spin}^{Gd_2}$	$MM_{orb}^{Gd_2}$	MM_{int}	$MM_{tot}^{Gd_1}$	$MM_{tot}^{Gd_2}$	MM_{tot}
$Pb_{1-x}Gd_xTiO_3$	$2 \times 2 \times 2$	6.94	7.34	0.02				0.40	7.36		7.95
$Pb_{1-x-\delta}Gd_xTiO_3$	$2 \times 2 \times 4$	6.93	6.99	0.02	6.93	6.99	0.02	0.12	7.01	7.01	13.91
$PbTi_{1-x}Gd_xO_{3-\delta}$	$2 \times 2 \times 4$	6.85	6.97	0.02	6.85	6.97	0.02	0.24	6.99	6.99	13.91

disorder will renormalize the ordered magnetization, while the effective paramagnetic moment remains close to the free-ion value of $7.9 \mu_B$. The finite- T evolution of these moments, their exchange couplings, and the resulting Curie temperatures are analyzed in Sec. II G, linking the zero-temperature benchmarks established here to experimentally relevant susceptibilities and magnetoelectric functionality.

D. Zero-temperature defect mechanisms and charge compensation in Gd-doped $PbTiO_3$

Defect energetics were evaluated from total energies within PBE-GGA + U including SOC, for both intrinsic vacancies stabilizing aliovalent doping and for the Gd impurity itself. Vacancy formation energies follow

$$E_f^{D=Vac.} = E_{tot}(\text{with vac}) - E_{tot}(\text{no vac}) + E_{atom}(\text{removed}), \quad (2)$$

where $E_{tot}(\text{with vac})$ and $E_{tot}(\text{no vac})$ are the total energies of doped supercells with and without a Pb or O vacancy, and E_{atom} is the energy of the removed atom. Vacancy/no-vacancy structures were constructed in identical $2 \times 2 \times 4$ cells to enhance cancellation of finite-size and basis-set errors. Impurity formation energies are computed as

$$E_f^{D=Imp.} = E_{tot}(\text{doped}) - E_{tot}(\text{host}) + \mu_{host} - \mu_{Gd}, \quad (3)$$

where $E_{tot}(\text{doped})$ and $E_{tot}(\text{host})$ are the total energies of doped and pristine $PbTiO_3$, and μ_{host} and μ_{Gd} denote the chemical potentials of the substituted atom (Pb or Ti) and of elemental Gd [13]. For the $2 \times 2 \times 4$ supercell, which contains two Gd dopants ($x = 0.125$), Eq. (3) is normalized per Gd atom, whereas no normalization is needed for $2 \times 2 \times 2$ cells with a single dopant. Additional computational details are provided in Sec. SM II I in Ref. [16].

The results in Table IV establish three points crucial to the design strategy of this work. First, uncompensated Gd substitution is strongly site selective: $E_f^{Imp.} = -2.03$ eV for Gd_{Pb} but +14.86 eV for Gd_{Ti} , confirming the thermodynamic preference for the A site (Pb) in agreement with ionic-size arguments and prior hybrid-DFT benchmarks [13]. Second, intrinsic defect compensation is energetically favorable in both chemistries: $Gd_{Pb} + V_{Pb}$ yields $E_f = -26.09$ eV and $Gd_{Ti} + V_O$ gives $E_f = -1.67$ eV, indicating that vacancies not only neutralize charge but also relieve elastic and electrostatic strain. Third, compensation reverses the otherwise prohibitive cost of Ti-site doping, rendering Gd_{Ti} viable only in the presence of V_O , consistent with the electronic-structure trends where V_O shifts Gd- f weight away from E_F and restores a gap (Secs. II C 1 and II C 2).

Energetic stabilization by V_{Pb} and V_O thus provides the thermodynamic foundation for the compensated semiconducting states analyzed throughout this paper: the DOS and band structures show gap reopening and reduced f -metallicity, the Bader analysis (Sec. II E) reveals strengthened Ti–O ionicity, and Berry phase calculations (Sec. II H) confirm large polarizations comparable to pristine $PbTiO_3$. Combined with the very weak intersite exchange extracted later (Table VI), these energetics rationalize a picture where robust local Gd^{3+} moments coexist with an insulating, polar lattice—multifunctional at room temperature (ferroelectric + paramagnetic) and multiferroic only below T_C^{MF} .

E. Bader electron charges, electronic redistribution, and ionicity trends in Gd-doped $PbTiO_3$

Bader charges were obtained from all-electron FP-APW + lo densities in WIEN2k [59–63] and postprocessed with CRITIC2 [64,65] within the QTAIm framework [57,58]. To monitor global consistency we define the stoichiometric neutralization (SN) as

$$SN = \sum_A (q_A - q_A^{nom}), \quad (4)$$

with $q_A^{nom} = \{+2, +4, -2, +3\}$ for $\{Pb, Ti, O, Gd\}$, respectively.

Table V shows SN values near zero for both compensated systems [$Pb_{0.8125}Gd_{0.125}TiO_3$ (V_{Pb}): -0.0284 ; $PbTi_{0.875}Gd_{0.125}O_{2.9375}$ (V_O): $+0.0021$], indicating effective electronic compensation when vacancies accompany aliovalent Gd^{3+} substitution. Notably, these values are smaller than those obtained previously for uncompensated models [13], confirming improved long-range stoichiometric neutralization.

The nature of local bonding is further examined by the absolute deviation $|\Delta q_A| = |q_A - q_A^{nom}|$, which captures the extent of charge localization or delocalization. Pb retains the smallest $|\Delta q|$ (~ 0.62 – 0.67), consistent with largely ionic Pb bonding. Ti exhibits the largest deviations (~ 1.69 – 1.83), and O shows sizable changes (~ 0.76 – 0.81), together evidencing Ti–O covalency in pristine $PbTiO_3$. Doping reduces this covalency in a site-selective way: the sum $|\Delta q_{Ti}| + |\Delta q_O|$ is lowest in Pb-site doping (2.45), intermediate in Ti-site doping (2.51), and highest in pristine $PbTiO_3$ (2.60). This hierarchy shows that both types of doping enhance Ti–O ionicity, but more strongly in the Pb-site case, correlating with its slightly higher tetragonality and polarization (Secs. II B, II H).

The dopant valence is likewise site-dependent. For Gd at Pb sites, $q_{dop} \approx 2.13$ ($\Delta q_{dop} = 0.87$), closer to trivalent

TABLE IV. Spin-polarized PBE-GGA + U (with SOC) total energies and corresponding defect formation energies $E_f^{(D)}$ (eV) for $x = 0.125$ doping, comparing uncompensated Gd substitution with charge-compensated configurations (V_{Pb} , V_{O}). Entries marked * are from this work using $2 \times 2 \times 4$ supercells; literature values use $2 \times 2 \times 2$ hybrid-DFT cells [13]. Reference elemental energies are listed for chemical potentials.

Compound/Element	Supercell	δ	Scheme	Total Energy (eV)	Gd Site	Defect Type	$E_f^{(D)}$ (eV)	Ref.
$\text{Pb}_{1-x-\delta}\text{Gd}_x\text{TiO}_3$	$2 \times 2 \times 4$	0.0625	PBE-GGA + U	-8487382.89	Pb	V_{Pb}	-26.09	*
$\text{PbTi}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$				-10147303.25	Ti	V_{O}	-1.67	*
$\text{Pb}_{1-x}\text{Gd}_x\text{TiO}_3$				-9056849.92	Pb		-2.034	*
$\text{PbTi}_{1-x}\text{Gd}_x\text{O}_3$				-10149347.34	Ti		14.86	*
PbTiO_3				-9581922.76				*
$\text{Pb}_{1-x}\text{Gd}_x\text{TiO}_3$	$2 \times 2 \times 2$	0.125	Hybrid	-4528423.88	Pb		-1.40	[13]
$\text{Pb}_{1-x}\text{Gd}_x\text{TiO}_{3-\delta}$				-4526369.40		V_{O}	8.75	[13]
$\text{PbTi}_{1-x}\text{Gd}_x\text{O}_3$				-5074669.70	Ti		18.38	[13]
$\text{PbTi}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$		0.125	PBE-GGA	-5072622.27		V_{O}	1.71	[13]
Gd				-306954.67				[13]
Pb				-569493.12				[13]
Ti				-23227.52				[13]
O				-2045.73				[13]

character than at Ti sites, where $q_{\text{dop}} \approx 1.99$ ($\Delta q_{\text{dop}} = 1.01$). These trends are consistent with orbital fingerprints in the DOS (Sec. II C 1) and with the gap reopening observed in Fig. 3.

Briefly, QTAIM/Bader analysis quantifies how charge compensation redistributes electron density to stabilize aliovalent doping: Pb remains largely ionic, Ti–O bonds become more ionic (Pb-site > Ti-site > pristine), and Gd ionicity is site sensitive. These metrics rationalize the semiconducting gaps (Secs. II C 1 and II C 2), the favorable formation energies (Sec. II D), and the persistence of large Berry phase polarization (Sec. II H), thereby linking atomic-scale charge topology to multifunctional ferroic behavior.

F. DFT- and SPM-based CF modeling of Gd^{3+} magnetism in PbTiO_3 systems

To connect defect stabilization (Sec. II D) and charge redistribution (Sec. II E) with magnetic response, the crystal field parameters (CFPs) of Gd^{3+} were determined using two complementary approaches: (i) first-principles projections of Gd 4f Wannier states (DFT + CFT) and (ii) semiempirical superposition model (SPM) fits [46]. Methodological details are provided in the Supplemental Material [16], while complete numerical datasets are reported in Appendix C.

Throughout this work, the terms *symmetry lowering* and *symmetry reduction* refer strictly to the *local site*

symmetry (point-group symmetry) of the Gd^{3+} coordination environment, not to a change in the global crystallographic symmetry. At dilute Gd concentrations, the average structure remains essentially tetragonal ($P4mm$), whereas the local symmetry at a given Gd site depends on the nearby charge-compensating defects; this distinction is key for interpreting low-symmetry effects in CF/EMR frameworks [92].

In Pb-site Gd substitution without charge-compensating vacancies, $\text{Pb}_{1-x}\text{Gd}_x\text{TiO}_3$, Gd substitutes at the Pb site with approximate C_{4v} local site symmetry, for which only the tetragonal symmetry-allowed CFPs occur, while nonaxial terms such as B_{22} , B_{42} , and B_{62} are forbidden. When a compensating Pb vacancy is present in the immediate coordination shell, the vacancy lies off the tetragonal fourfold axis: the $90^\circ/270^\circ$ rotational symmetry elements and two vertical mirror planes are broken, reducing the local site symmetry from C_{4v} to C_{2v} . This activates nonaxial CFPs (B_{22} , B_{42} , B_{62}), thereby linking defect-induced distortions to anisotropic 4f-shell magnetism (Appendix C).

For Ti-site substitution, the local symmetry outcome depends on vacancy position. An apical O1 vacancy lies on the tetragonal axis and can preserve the principal symmetry elements (approximately C_{4v}), whereas an equatorial O2 vacancy lies off axis and breaks the fourfold symmetry in a manner analogous to the Pb-vacancy case, thus lowering the

TABLE V. Bader electrons q_A (in e) for Pb, Ti, O, and Gd in pristine PbTiO_3 and in doped compositions at $x = 0.125$ with vacancy levels $\delta = 0.0625$ or 0.125 . Deviations $|\Delta q_A|$ are taken from nominal ionic charges (Pb^{2+} , Ti^{4+} , O^{2-} , Gd^{3+}). The dopant charge q_{dop} and its deviation Δq_{dop} are reported, together with the stoichiometric neutralization (SN), which quantifies the net charge imbalance per formula unit (f.u.). Values marked * are from this work; others from Ref. [13].

Compound	δ	q_{Pb}	$ \Delta q_{\text{Pb}} $	q_{Ti}	$ \Delta q_{\text{Ti}} $	q_{O}	$ \Delta q_{\text{O}} $	q_{dop}	Δq_{dop}	SN	Ref.
$\text{Pb}_{1-x-\delta}\text{Gd}_x\text{TiO}_3$	0.0625	+1.3714	0.6286	+2.3071	1.6929	-1.2386	0.7614	+2.1300	0.8700	-0.0284	*
$\text{PbTi}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$	0.0625	+1.3522	0.6478	+2.2604	1.7396	-1.2255	0.7745	+1.9905	1.0095	0.0021	*
PbTiO_3		+1.3815	0.6185	+2.2043	1.7957	-1.1947	0.8053			0.0017	[13]
$\text{Pb}_{1-x}\text{Gd}_x\text{TiO}_3$		+1.3754	0.6246	+2.1759	1.8241	-1.2316	0.7684	+2.2798	0.7202	-0.0304	[13]
$\text{PbTi}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$	0.125	+1.3306	0.6694	+2.1706	1.8294	-1.1994	0.8006	+1.9751	1.0249	0.028	[13]

TABLE VI. Exchange constant J and mean-field Curie temperature T_C^{MF} for compensated Gd-doped PbTiO_3 , obtained by mapping FM–AFM total-energy differences onto a nearest-neighbor Heisenberg model [Eqs. (5) and (6)]. Both systems yield $J \sim 10^{-3}$ meV, corresponding to $T_C^{\text{MF}} < 1$ K, consistent with paramagnetism under ambient conditions.

Compound	J (meV)	T_C^{MF} (K)
$\text{Pb}_{0.8125}\text{Gd}_{0.125}\text{TiO}_3$	0.0015	1.11
$\text{PbTi}_{0.875}\text{Gd}_{0.125}\text{O}_{2.9375}$	0.0010	0.85

site symmetry and, in principle, allowing additional nonaxial CFP components.

Importantly, lowering the local symmetry from C_{4v} to C_{2v} does not merely renormalize existing axial CFPs; it changes the allowed tensor structure of the CF Hamiltonian by enabling additional symmetry-allowed terms. These terms generate transverse anisotropy in the $\mathbf{g}$ tensor and Van Vleck [93] susceptibility tensor components, providing robust fingerprints of vacancy-associated local symmetry breaking even when the global crystal symmetry remains tetragonal.

In real materials, dopants and compensating vacancies are expected to be distributed in a largely disordered manner. Such disorder does not restore higher local site symmetry at vacancy-adjacent Gd^{3+} sites; instead, each site retains its locally reduced symmetry while the orientations of the corresponding low-symmetry axes vary from site to site. Consequently, CF eigenvalues and level splittings remain characteristic of each defect motif, defined here as a specific local dopant-vacancy configuration and coordination geometry around a Gd^{3+} ion, which uniquely determines its local point symmetry and crystal-field Hamiltonian. Macroscopic tensor observables, by contrast, reflect configurational and orientational averaging over many such locally equivalent but differently oriented motifs.

Notably, this local symmetry reduction strongly affects crystal-field anisotropy and magnetic response, while the global symmetry channel responsible for ferroelectric polarization remains intact (subsection of Sec. II H).

Across all configurations, the dominant axial CFP B_{20} is large and negative (~ -700 to -1400 cm^{-1}), consistent with tetragonal distortions of Ti-O polyhedra in PbTiO_3 and favoring easy-plane magnetism. Higher-rank CFPs (B_{44} , B_{64}) introduce transverse anisotropies of the $\mathbf{g}$ and magnetic-susceptibility tensors, with magnitudes comparable to those reported for benchmark Gd phosphates and vanadates [88]. In vacancy-stabilized $\text{Pb}_{1-x}\text{Gd}_x\text{TiO}_3$, symmetry reduction to C_{2v} induces otherwise forbidden CFPs (B_{22} , B_{42} , B_{62}), directly linking structural distortions to anisotropic magnetism. Representative magnitudes (DFT) include $B_{22} \sim 150 \text{ cm}^{-1}$ at the Gd1 site, with SPM variants yielding $B_{22} \sim 100 - 130 \text{ cm}^{-1}$, confirming robust nonaxial CF fingerprints of $C_{4v} \rightarrow C_{2v}$ symmetry lowering (Table VII).

To choose a transferable semiempirical alternative, we benchmarked SPM(a), SPM($b^\pm$), SPM($c^\pm$) against DFT-derived CFPs using the RMSE, $\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^n (B_{kq}^{\text{DFT}} - B_{kq}^{\text{SPM}})^2}$, and found that SPM(b^-) (intrinsic

$\bar{A}_k$ reduced by 20%) gives the lowest RMSE for most crystallographically distinct Gd sites while reproducing the sign and magnitude of the key axial CFPs (B_{20} , B_{40} , B_{60}). We therefore adopt SPM(b^-) for quantitative predictions where efficiency is critical; site-refined SPM($c^\pm$) remains reliable when local distortions are large (see Secs. SM II B, SM III I in Ref. [16]).

To elucidate the CF level splittings and anisotropic responses we employed two complementary approaches: DFT + CFT + Δ + Zeem.+Reg. and SPM(b^-)+CFT + Zeem.+Reg. Here, $\Delta = -0.6$ Ry accounts for $4f$ -ligand hybridization (Sec. SM III K in Ref. [16]), “Zeem.” denotes explicit the Zeeman interaction term in the CF Hamiltonian, and “Reg.” indicates the regularization enforcing Kramers degeneracy (Secs. SM II A, SM III J–K in Ref. [16], and Ref. [25]). Importantly, the $\mathbf{g}$ tensor and Van Vleck susceptibilities reported in Table VIII are not free parameters but follow directly from the field-dependent eigenenergies, as expressed in Eq. (A4), so that g_i and χ_i^{VV} are determined by quadratic regression of $\varepsilon_i(\mathbf{B})$ versus $\mathbf{B}$. This step incorporates both spin-orbit coupling and crystal-field interaction that induce the anisotropy of the $\mathbf{g}$ due to spin-orbit coupling and crystal-field interaction and magnetic susceptibility into experimentally relevant observables, linking microscopic CFPs to macroscopic response functions.

Diagonalization of Eq. (A2) shows the $^8S_{7/2}$ ground multiplet splits into four Kramers doublets with $\varepsilon_i(0) \sim 0.01 - 0.5 \text{ meV}$ (Table VIII). Despite these small splittings (expected for $L = 0$), the $\mathbf{g}$ tensor is strikingly anisotropic: at Pb sites $g_{1\perp} \sim 13$ while $g_{1\parallel} \ll 1$, confirming robust easy-plane behavior; O vacancies at Ti sites enhance splittings (up to $\sim 0.48 \text{ meV}$) and yield site-selective anisotropies of $\mathbf{g}$ tensor and magnetic susceptibility. Van Vleck susceptibilities mirror this pattern, with $\chi_{\perp}^{\text{VV}} \gg \chi_{\parallel}^{\text{VV}}$, demonstrating large directional responses that persist into the paramagnetic regime.

Three conclusions follow. *First*, intrinsic vacancies not only stabilize aliovalent doping (Sec. II D) but also affect anisotropies of $\mathbf{g}$ tensor and magnetic susceptibility on the f -shell manifold via symmetry lowering (leading to activation of the nonaxial CFPs B_{22} , B_{42} , B_{62}). *Second*, the quantitative agreement between DFT + CFT + Δ + Zeem.+Reg. and SPM(b^-)+CFT + Zeem.+Reg. validates the semiempirical route for efficient large-scale predictions. *Third*, the anisotropic $\mathbf{g}$ tensors and susceptibilities rationalize the robust paramagnetism above T_c (Table VI) and connect directly to the finite-temperature analysis in Sec. II G.

Together with the polarization results of Sec. II H, these findings show how vacancy-engineered crystal fields couple localized f -shell moments to ferroelectric distortions, enabling tunable magnetoelectric responses in rare-earth-doped PbTiO_3 .

G. Crystal-field-controlled magnetism and finite-temperature optical redshift in Gd-doped PbTiO_3

Sections II C 4, II C 1, and II D established that charge-compensated Gd substitution in PbTiO_3 stabilizes nearly atomic, spin-only $4f^7$ moments ($\sim 7.0 \mu_B$ per Gd when interstitial contributions are included) while maintaining an insulating, polarized host. Here we bridge this $T = 0$

defect-stabilized picture to finite temperature, where the key issue is not the existence of local moments but whether they can develop collective order and how their thermal disorder feeds back into the electronic/optical response. Two complementary ingredients govern the finite- T behavior: (i) ultraweak intersite exchange and (ii) single-ion crystal-field (CF) effects, which control the anisotropic $\mathbf{g}$ tensor and Van Vleck response (Sec. II F). Accordingly, we combine (i) a Heisenberg mapping of FM–AFM total-energy differences to extract J and T_C^{MF} , and (ii) a CF-based thermodynamic treatment in which DFT + Δ /SPM + CFT multiplets are Zeeman-split, thermally populated, and averaged to obtain $M(T, \mathbf{B})$ [Eq. (SM13)] and $\chi(T)$ (Eq. (SM13) in Ref. [16]).

Within mean-field theory [94],

$$T_C^{\text{MF}} = \frac{(S+1) 2zJS^2}{3S k_B}, \quad (5)$$

where $S = 7/2$ for Gd^{3+} , z is the nearest-neighbor coordination, and J is defined through the isotropic Heisenberg Hamiltonian

$$\hat{H}_{\text{ex}} = \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (J_{ij} = J_{ji}), \quad (6)$$

with $J > 0$ ($J < 0$) corresponding to ferro- (antiferro-) coupling. Mapping the FM–AFM energy difference $\Delta E = E_{\text{AFM}} - E_{\text{FM}}$ (treating the six tetragonal A/B neighbors as equivalent) yields

$$J = \frac{\Delta E}{4S(S+1)}. \quad (7)$$

Table VI shows that both compensated configurations— $\text{Pb}_{0.8125}\text{Gd}_{0.125}\text{TiO}_3$ ($\text{Gd}_{\text{Pb}} + \text{V}_{\text{Pb}}$) and $\text{PbTi}_{0.875}\text{Gd}_{0.125}\text{O}_{2.9375}$ ($\text{Gd}_{\text{Ti}} + \text{V}_{\text{O}}$)—yield $J \simeq 10^{-3}$ meV and hence $T_C^{\text{MF}} \lesssim 1$ K. Because mean-field theory overestimates ordering, the true ordering temperature (if any) is even lower. Thus, despite robust $4f^7$ moments, long-range magnetic order is excluded at laboratory temperatures. The extracted couplings are negligible compared to magnetic titanates such as GdTiO_3 ($T_C \sim 30\text{--}36$ K) [95,96] or EuTiO_3 ($T_N = 5.5$ K) [97]. This ultraweak exchange is also consistent with the compensated systems remaining semiconducting (Fig. 3), which suppresses carrier-mediated exchange channels. Notably, the same charge-compensation mechanisms that minimize defect formation energies at $T = 0$ also maximize the (still tiny) residual exchange by preventing metallization, underscoring charge compensation as a common lever for lattice stability and magnetic coupling.

The smallness of J can be understood microscopically from the symmetry and orbital character of Gd^{3+} in a perovskite host. (i) Gd^{3+} is a half filled $4f^7$ ion with $L = 0$, implying a nearly spherical $4f$ charge distribution and strongly localized orbitals. Consequently, symmetry-allowed virtual hopping processes involving $4f$ states are intrinsically weak, and the superexchange scale J (schematically $J \sim t^2/U$) is suppressed by both small effective hopping t and large on-site energy denominators. (ii) The perovskite geometry further reduces t : the relevant exchange paths are long and indirect (e.g., $\text{Gd}\text{--}\text{O}\text{--}\text{Ti}\text{--}\text{O}\text{--}\text{Gd}$ or vacancy-perturbed variants), with bond angles and separations that are unfavorable for strong overlap. This stands in sharp contrast to

transition-metal perovskites, where relatively delocalized d orbitals and near- 180° metal–O–metal bridges enable strong superexchange. (iii) The tetragonal polar environment and nearby defects primarily generate *single-ion* effects: local CF terms that control anisotropy (Sec. II F) rather than providing a mechanism for sizable isotropic, long-range coupling.

This separation of energy scales motivates an effective-spin description dominated by local physics,

$$\hat{H}_{\text{eff}} = \sum_i (\hat{H}_{\text{CF}}^{(i)} + \hat{H}_{\text{Zeem}}^{(i)}) + \sum_{\langle i,j \rangle} J \mathbf{S}_i \cdot \mathbf{S}_j, \quad (8)$$

where $\hat{H}_{\text{CF}}^{(i)}$ encodes the vacancy- and site-dependent CF environment (and hence anisotropic $\mathbf{g}$ tensors and Van Vleck susceptibilities), while the exchange interaction term is negligible on thermal scales above ~ 1 K. In this regime the Gd moments behave as essentially noninteracting $S = 7/2$ spins embedded in a polar host: weakly anisotropic at low T due to CF splittings, and Curie-like once $k_B T$ exceeds these splittings. Antisymmetric exchange is likewise negligible. Although local inversion symmetry can be broken by nearby vacancies—formally allowing a Dzyaloshinskii–Moriya interaction (DMI) [98,99]—the microscopic conditions required for an appreciable DMI are not satisfied in Gd-doped PbTiO_3 . In general, the DMI contribution to the magnetic Hamiltonian can be written as [98–102]

$$\hat{H}_{\text{DMI}} = \sum_{\langle i,j \rangle} \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j), \quad (9)$$

where the DMI vector $\mathbf{D}_{ij}$ arises from spin-orbit–assisted virtual hopping between neighboring magnetic ions in a noncentrosymmetric environment. In the present system, however, the highly localized and nearly spherical $4f^7$ electronic configuration of Gd^{3+} , weak $4f$ –ligand hybridization, and large Gd–Gd separations strongly suppress such spin-orbit–mediated exchange pathways. As a result, the DMI energy scale is expected to satisfy the strict hierarchy $|\mathbf{D}_{ij}| \ll J \ll k_B T$, where the already tiny isotropic exchange constant ($J \sim 10^{-3}$ meV) is itself far below thermal energies at any experimentally relevant temperature. Consequently, antisymmetric exchange plays no role in stabilizing collective magnetic order, and the magnetic response is dominated by single-ion crystal-field anisotropy, with both symmetric and antisymmetric intersite couplings strongly disfavored by symmetry and geometry.

The CF-based thermodynamic response was computed using the DFT + Δ /SPM + CFT + Zeeman + Boltzmann framework, where the $T = 0$ multiplets (Sec. II F) are Zeeman-split and thermally populated to obtain $M(T, \mathbf{B})$ and $\chi(T)$. Figures 5(a)–5(d) show the perpendicular ($M_\perp$) and parallel ($M_\parallel$) magnetizations under $\mathbf{B} = 0.1$ T, while Figs. 5(e)–5(h) compare them with Brillouin behavior for noninteracting $J = 7/2$, $g = 2$ spins (Eq. (S16) of Ref. [25]). At $T \lesssim 10$ K, measurable deviations from Brillouin curves occur, most prominently in $M_\parallel$ for Gd1 in $\text{Pb}_{0.8125}\text{Gd}_{0.125}\text{TiO}_3$ and in $M_\perp$ for Gd2 in $\text{PbTi}_{0.875}\text{Gd}_{0.125}\text{O}_{2.9375}$. These deviations directly reflect local CF anisotropy (encoded by the leading tetragonal CFPs such as B_{20} and B_{40} , and defect-activated terms where present; Sec. II F) rather than intersite correlations. In contrast, above $T \gtrsim 100$ K all magnetization

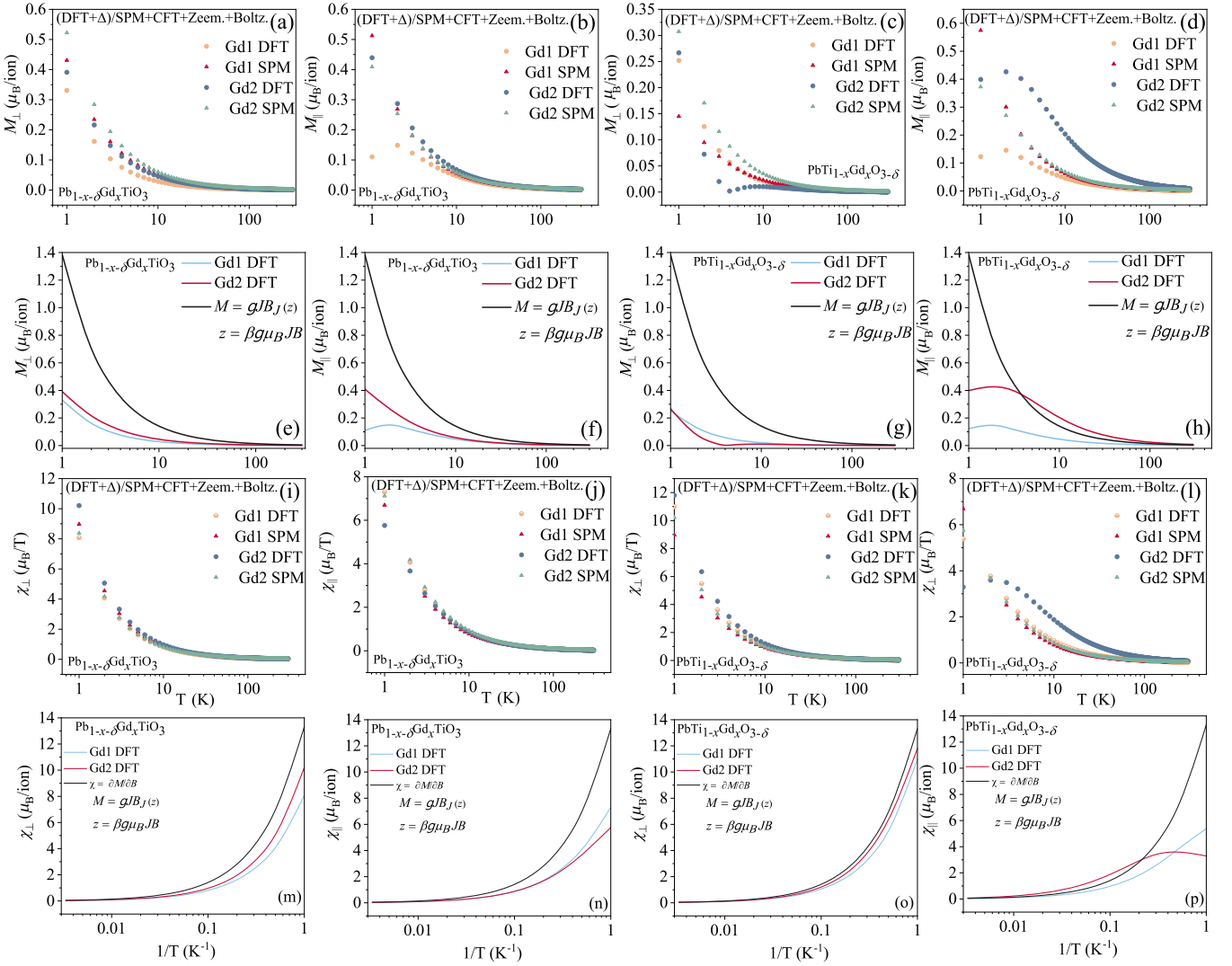


FIG. 5. Temperature-dependent magnetization and susceptibility of Gd^{3+} in compensated PbTiO_3 calculated from DFT + Δ /SPM + CFT + Zeeman + Boltzmann averaging under $B = 0.1$ T. (a)–(d) show perpendicular ($M_\perp$) and parallel ($M_\parallel$) magnetizations per Gd ion. (e)–(h) compare these results with Brillouin predictions ($J = 7/2$, $g = 2$), highlighting low- T anisotropy and the collapse of all curves to $M \sim 10^{-3} \mu_B/\text{ion}$ above $T \gtrsim 100$ K, consistent with ultraweak exchange ($J \sim 10^{-3}$ meV). (i)–(l) present the corresponding perpendicular ($\chi_\perp$) and parallel ($\chi_\parallel$) susceptibilities, and (m)–(p) show inverse-temperature plots revealing the crossover from anisotropic low- T response to Curie-like $1/T$ scaling above ~ 100 K, confirming paramagnetism with intact $4f^7$ moments.

curves collapse to $M \sim 10^{-3} \mu_B/\text{ion}$, consistent with thermal disordering of essentially independent moments and the vanishingly small J .

The corresponding susceptibilities $\chi_\perp$ and $\chi_\parallel$ [Figs. 5(i)–5(l)] display the same hierarchy of scales. At low T , χ deviates from a pure Curie law and exhibits anisotropy, reflecting CF-induced level structure and Van Vleck contributions. At higher T , all curves approach Curie-like scaling, reaching $\chi \sim (2 - 3) \times 10^{-2} \mu_B/T$ near 300 K. The inverse-temperature plots [Figs. 5(m)–5(p)] highlight the crossover to $1/T$ behavior above ~ 100 K, confirming paramagnetism with intact $4f^7$ moments.

Finally, this magnetic crossover provides the microscopic basis for the finite- T optical redshift (Sec. II C 3). As temperature increases, the progressive disordering of Gd moments reduces any residual exchange-induced spin splitting near the

band edges, lowering the absorption onset by ~ 0.2 – 0.4 eV, consistent with experiment [103]. Importantly, this magnetic disordering occurs in a host whose ferroelectric polarization remains nearly pristine in both compensated configurations (Sec. II H), demonstrating the coexistence of robust f moments, preserved ferroelectricity, and tunable band edges.

Overall, the finite- T analysis yields a unified picture: (i) nearly atomic $4f^7$ moments persist; (ii) exchange is ultraweak ($J \sim 10^{-3}$ meV), precluding collective magnetic order above ~ 1 K; (iii) low- T anisotropies originate from single-ion CF effects rather than intersite correlations; and (iv) thermal disorder of these moments naturally explains the observed optical-gap redshift while leaving ferroelectric polarization essentially intact. This compensation-stabilized balance identifies Gd-doped PbTiO_3 as a promising platform for devices that combine polarization stability with controlled

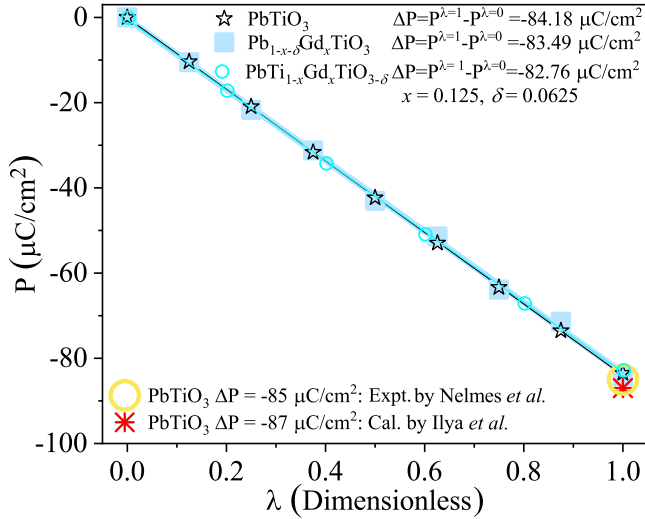


FIG. 6. Spontaneous polarization ΔP computed using the Berry-phase method for pristine PbTiO_3 , $\text{Pb}_{1-x}\text{Gd}_x\text{TiO}_3$ ($\text{Gd}_{\text{Pb}} + \text{V}_{\text{Pb}}$), and $\text{PbTi}_{1-x}\text{Gd}_x\text{TiO}_{3-\delta}$ ($\text{Gd}_{\text{Ti}} + \text{V}_{\text{O}}$) at $x = 0.125$ and $\delta = 0.0625$. Results are benchmarked against experimental [1] and theoretical [104] values for pristine PbTiO_3 . Further methodological details are given in Fig. 15 of Ref. [56] and in Ref. [15], Sec. 5.4 and Fig. SM6 [16].

paramagnetic response and band-edge engineering at room temperature.

H. Interplay of charge redistribution, defect configuration, magnetic moment, and orbital hybridization in stabilizing multifunctionality in Gd-doped PbTiO_3

Figure 6 demonstrates that both Pb-site and Ti-site charge-compensated Gd-doped systems preserve nearly pristine ferroelectric polarization. The computed values, $\Delta P = -83.5$ and $-82.8 \mu\text{C}/\text{cm}^2$, differ by less than 2% from pristine PbTiO_3 ($-84.2 \mu\text{C}/\text{cm}^2$) and are in excellent agreement with experiment ($-85 \mu\text{C}/\text{cm}^2$ [1]). This robustness of polarization under aliovalent substitution is a key result of this work.

The modest reduction in ΔP closely tracks the reduction in tetragonality induced by doping. As summarized in Table I, the c/a ratio decreases from 1.066 in pristine PbTiO_3 to 1.058 for Pb-site doping and 1.055 for Ti-site doping. Importantly, this reduction does not signal degradation of ferroelectricity; rather, it reflects a mechanically stabilized lattice in which charge-compensated substitution relieves internal strain while preserving the polar distortion. Thus, structural robustness and ferroelectric functionality are achieved simultaneously.

To elucidate the microscopic mechanisms underlying this behavior, we analyze charge redistribution using Bader partitioning (Sec. II E). Pb-site substitution yields stronger Ti–O ionicity, quantified by $|\Delta q_{\text{Ti}}| + |\Delta q_{\text{O}}| = 2.45$, but exhibits a slight deviation from perfect global stoichiometric neutralization ($\text{SN} = -0.0284$). In contrast, Ti-site substitution achieves near-ideal stoichiometric neutralization ($\text{SN} = +0.0021$) but with somewhat weaker Ti–O polarity (2.51). These results show that polarization correlates more strongly with *local bond ionicity* than with global charge neutrality: the enhanced Ti–O polarity in the Pb-site-doped system sustains the largest ΔP despite its small charge imbalance.

The dopant itself participates asymmetrically in this compensation. Gd exhibits a more trivalent-like character at the Pb site ($\Delta q_{\text{dop}} = 0.87$) than at the Ti site (1.01), reinforcing the site-dependent nature of charge redistribution. Taken together, these findings reveal two complementary stabilization pathways: ionicity-driven polarization at the Pb site and stoichiometric-neutralization-driven stabilization at the Ti site. Both mechanisms support robust ferroelectricity, consistent with the strongly favorable formation energies discussed in Sec. II D.

Projected density of states (Sec. II C 1) further clarifies the microscopic origin of polarization. In pristine PbTiO_3 , ferroelectricity is driven by Pb $6s - 6p$ lone-pair hybridization near -1 eV . Upon Gd doping, this lone-pair feature is suppressed. Simultaneously, a new mechanism emerges: enhanced Ti–O ionicity mediated by Gd $4f - \text{Ti } 3d - \text{O } 2p$ hybridization in the -6 to -4 eV energy window. Bader charges corroborate this picture by showing reduced deviations of Ti and O charges from their nominal ionic values, signaling a shift toward stronger Ti–O polarity. Thus, aliovalent substitution induces a qualitative change in the microscopic origin of ferroelectricity—from lone-pair-driven to ionicity-assisted hybridization—while preserving the macroscopic polar order.

The coexistence of large spontaneous polarization ΔP with well-localized $4f^7$ Gd moments establishes a polar magnetic ground state in Gd-doped PbTiO_3 . While the ferroelectric order is robust and persists up to the high ferroelectric Curie temperature associated with the tetragonal-to-cubic structural transition, the magnetic sector is governed by ultraweak inter-site exchange interactions. Our total-energy mapping yields $J \sim 10^{-3} \text{ meV}$, corresponding to a mean-field magnetic ordering temperature $T_{\text{C}}^{\text{MF}} < 1 \text{ K}$, which should be regarded as an upper bound. Given the known overestimation inherent to mean-field theory and the absence of strong exchange pathways, long-range magnetic order is not expected at any experimentally accessible temperature.

Consequently, for all practical temperatures the system realizes a polar paramagnetic state: ferroelectric order remains intact, while Gd moments are thermally disordered but retain their large single-ion character. Although this regime is not multiferroic in the strict sense of coexisting long-range ferroic orders, it remains functionally coupled. Charge redistribution, crystal-field-induced anisotropy of the $\mathbf{g}$ tensor and magnetic susceptibility, and exchange-suppressed spin disorder are all governed by the same underlying electronic structure. These couplings also underpin the finite-temperature optical redshift discussed in Sec. II C 3.

Robust ferroelectricity under local site symmetry breaking

The persistence of near-pristine polarization despite strong local structural and electronic perturbations raises an important symmetry question. From a symmetry perspective, macroscopic ferroelectricity in PbTiO_3 is governed by the *global space-group symmetry* rather than by the local site symmetry of individual cations. In pristine PbTiO_3 , ferroelectricity originates from the unstable Γ_{15} polar soft mode of the cubic perovskite phase, which condenses into the A_1 irreducible representation in the tetragonal $P4mm$ structure

[105]. As long as the global crystal symmetry remains polar and permits this $\Gamma_{15} \rightarrow A_1$ distortion, a nonzero macroscopic polarization is symmetry-allowed.

At dilute Gd concentrations, the average crystallographic symmetry remains tetragonal, and the global polar order-parameter channel is therefore preserved. Local symmetry breaking at the Pb site—induced by aliovalent Gd substitution and/or nearby charge-compensating vacancies—reduces the local point-group symmetry and perturbs the immediate atomic environment. Crucially, however, these local perturbations do not eliminate or forbid the global $\Gamma_{15} \rightarrow A_1$ polar distortion dictated by the space group. Instead, they primarily modulate the *local amplitude* and spatial distribution of polar displacements, while the existence of long-range ferroelectric order remains protected by symmetry.

This distinction between global and local symmetry channels is directly borne out by our structural and polarization results. The tetragonal distortion persists across all doped configurations, with c/a ratios remaining significantly larger than unity. Berry-phase calculations (Fig. 6) show that ΔP is reduced by less than 2% upon doping, in excellent agreement with experiment. Bond-orientation and atomic-displacement, as shown in Figs. 1(b) and 1(c), analyses further confirm that Pb–O and Ti–O displacements remain predominantly aligned along the tetragonal c axis, demonstrating coherent alignment of local polar shifts with the global polarization direction.

Importantly, this symmetry-based separation explains the coexistence of robust ferroelectricity with strongly anisotropic magnetism. While local symmetry reduction has only a secondary, quantitative effect on the ferroelectric order parameter, it has a pronounced qualitative impact on the crystal-field Hamiltonian of Gd^{3+} , leading to activation of otherwise forbidden nonaxial CFPs and strongly enhancing $\mathbf{g}$ tensor and susceptibility anisotropies (Sec. II F). Thus, local symmetry breaking serves as an effective tuning knob for magnetic anisotropy and paramagnetic response, while the global symmetry channel responsible for macroscopic polarization remains intact. Together, symmetry arguments, tetragonal distortions, Berry-phase polarization, charge redistribution, and magnetic anisotropy form a unified and compelling explanation for the survival of ferroelectricity and the emergence of multifunctionality in Gd-doped PbTiO_3 .

III. CONCLUSIONS

We have established a symmetry-consistent and defect-aware microscopic framework for understanding how aliovalent rare-earth substitution, charge compensation, and local structural symmetry breaking collectively govern the structural, electronic, magnetic, and optical properties of the displacive ferroelectric Gd-doped PbTiO_3 . By integrating first-principles electronic-structure calculations with Berry-phase polarization, defect thermodynamics, Wannier-based crystal-field extraction, superposition modeling, and finite-temperature statistical mechanics, we reconcile theory and experiment while uncovering general organizing principles relevant to doped ferroelectric oxides.

A major outcome of this work is the resolution of the long-standing discrepancy between earlier first-principles predictions of metallic behavior and experimental observations

of insulating Gd-doped PbTiO_3 . We demonstrate that this discrepancy does not originate from the choice of exchange-correlation functional alone, but from neglecting intrinsic charge compensation. Aliovalent Gd^{3+} substitution destabilizes the insulating ground state unless compensated by Pb or O vacancies. Once charge neutrality is restored, both Pb-site and Ti-site substitutions yield negative formation energies, finite band gaps, and robust ferroelectric polarization. This establishes defect-controlled charge balance as the decisive microscopic mechanism stabilizing the insulating ferroic phase.

Importantly, we show that the persistence of macroscopic ferroelectricity under aliovalent substitution is symmetry protected. While Gd substitution and compensating vacancies strongly reduce the local point symmetry and modify local displacement amplitudes, the global tetragonal $P4mm$ symmetry remains polar and continues to support the $\Gamma_{15} \rightarrow A_1$ displacive ferroelectric distortion. As a result, the spontaneous polarization remains within $\sim 2\%$ of pristine PbTiO_3 values, despite modest reductions in tetragonality. Bader charge analysis reveals that this robustness is sustained by complementary stabilization mechanisms: enhanced Ti–O ionicity that preserves off-centering and near-stoichiometric charge neutrality that suppresses spurious metallicity. These results clarify, at a fundamental level, why long-range ferroelectric order survives strong local site symmetry breaking.

At the magnetic level, Gd^{3+} ions retain nearly atomic $4f^7$ spin-only moments. Vacancy-induced local site symmetry reduction activates nonaxial crystal-field parameters and generates pronounced $\mathbf{g}$ -tensor and susceptibility anisotropies, providing quantitative fingerprints of the defect environment. However, intersite magnetic exchange is intrinsically suppressed: the spherical $4f^7$ charge distribution ($L = 0$), unfavorable superexchange geometries in the perovskite lattice, and large Gd–Gd separations yield exchange constants of order 10^{-3} meV and a mean-field Curie temperature below 1 K. Consequently, long-range magnetic order is excluded at experimentally relevant temperatures, and the magnetic degrees of freedom are governed by single-ion physics rather than cooperative interactions.

This places Gd-doped PbTiO_3 in a regime that is *strictly multiferroic only below a vanishingly small magnetic ordering temperature*, but *multifunctional under all practical conditions*. Robust ferroelectric polarization coexists with stable, localized paramagnetic moments without invoking strong magnetoelectric coupling. This distinction is essential: the present work does not claim emergent room-temperature multiferroicity, but instead establishes how symmetry-protected ferroelectric order can coexist with localized f -electron magnetism in the absence of magnetic ordering.

Finally, we demonstrate that magnetic disorder feeds back into the electronic structure at finite temperature. Thermal spin disorder reduces exchange splittings at the band edges, producing an optical-gap redshift of ~ 0.2 – 0.4 eV that complements conventional electron-phonon renormalization. Defect configuration further enables bidirectional band-gap tuning: Ti-site Gd with O vacancies narrows the gap, whereas Pb-site Gd with Pb vacancies widens it, while both remain insulating. This unifies lattice stabilization, suppression of long-range magnetism, and finite-temperature

optoelectronic response within a single microscopic framework.

In summary, Gd-doped PbTiO₃ emerges as a prototypical compensation-engineered perovskite in which global symmetry protects displacive ferroelectric order, local site symmetry controls single-ion magnetism, and defects govern electronic topology. Beyond addressing a specific theory–experiment contradiction, this work lays out general, transferable principles for understanding and designing aliovalently doped ferroelectrics with combined structural, magnetic, and optical functionalities. These principles are broadly relevant to defect physics, correlated oxides, and symmetry-controlled multifunctional materials.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this article are openly available [106].

APPENDIX A: THEORETICAL METHODOLOGIES

To describe the multifunctional response of Gd-doped PbTiO₃, we employed a unified theoretical framework combining density functional theory (DFT), CFT, SPM, quasiparticle band-gap corrections, topological charge analysis, and Berry-phase polarization theory. This approach connects local defect chemistry and bonding topology to magnetic anisotropy, electronic structure, and ferroelectric polarization.

1. CF modeling and magnetic anisotropy

The magnetic response of Gd³⁺ was treated by combining DFT [107,108] with CFT [20,21] and the SPM [22]. In the DFT + CFT approach, the Gd 4*f* shell is first frozen into the core to suppress self-interaction errors [26], after which a non-self-consistent calculation with 4*f* states in the valence is performed. Projection onto maximally localized Wannier functions (WIEN2WANNIER/WANNIER90) [30–34] yields a 7 × 7 on-site Hamiltonian $\hat{H}_{4f}$, from which the CF Hamiltonian is obtained as [26]

$$\hat{H}_{\text{CF}} = \hat{H}_{4f} - E_{\text{avg}}\hat{I}, \quad E_{\text{avg}} = \frac{1}{7}\text{Tr}(\hat{H}_{4f}), \quad (\text{A1})$$

and expanded in Wybourne-normalized tensor operators [21],

$$\hat{H}_{\text{CF}} = \sum_{k=0}^6 \sum_{q=-k}^k B_{kq} \hat{C}_q^{(k)}, \quad (\text{A2})$$

where B_{kq} are the CFPs in the Wybourne notation [21,26].

Complementarily, the SPM expresses CFPs as geometry-driven ligand contributions [22],

$$B_{kq} = \sum_i \bar{A}_k \left(\frac{R_0}{R_i} \right)^{t_k} K_{kq}(\theta_i, \phi_i), \quad (\text{A3})$$

providing an efficient description of low-symmetry environments and vacancy-induced distortions. Methodological details and benchmarks between DFT + CFT and SPM + CFT are given in the SM (Sec. SM II A2) [16].

Magnetic anisotropy arises from the combined action of CFs and external magnetic fields $\mathbf{B}$, leading to anisotropic Zeeman splitting of Kramers doublets [25],

$$\varepsilon_i(\mathbf{B}) = \varepsilon_i(0) \pm \frac{1}{2}\mu_B \mathbf{B} \cdot \mathbf{g}_i(\hat{\mathbf{n}}) - \frac{1}{2}\mathbf{B} \cdot \chi_i^{\text{vV}} \cdot \mathbf{B}, \quad (\text{A4})$$

where $\mathbf{g}_i$ and χ_i^{vV} are the effective $\mathbf{g}$ tensor and Van Vleck susceptibility tensor, respectively. The thermally averaged magnetic moment follows as

$$M_v(T) = \frac{\sum_i m_{i,v} e^{-\varepsilon_{i,v}/k_B T}}{\sum_i e^{-\varepsilon_{i,v}/k_B T}}, \quad (\text{A5})$$

from which $\chi_v(T)$ is obtained. Detailed derivations are provided in the SM (Secs. SM II B–SM II P [16] and Refs. [109–112].

2. Electronic and optical band gaps, charge redistribution, and polarization

To address the well-known band-gap underestimation of standard DFT [48–53], electronic gaps were refined using the Tran-Blaha modified Becke-Johnson (TB-mBJ) potential [48,49] and its JTSKTB-mBJ extension for correlated oxides [54]. Optical gaps were obtained from the dielectric function within the random-phase approximation combined with Tauc analysis [55],

$$E_g^{\text{opt}} = \hbar\omega - \frac{(\alpha\hbar\omega)^{1/\gamma}}{B}, \quad (\text{A6})$$

with $\gamma = 1/2$ (direct) or 2 (indirect). This framework directly links quasiparticle-corrected electronic structure to experimentally accessible absorption onsets (see SM, Secs. SM II C and SM II K) [16].

Bonding and charge redistribution were analyzed using the Quantum Theory of Atoms in Molecules (QTAIM) [57,58,66,67], applied to all-electron charge densities obtained from FP-APW + lo calculations. Bader electron charges quantify changes in Ti–O ionicity, Pb lone-pair activity, and local charge compensation induced by Gd substitution and vacancies. Technical details are provided in the SM (Secs. SM II D and SM II M) [16].

Ferroelectric polarization was evaluated using the Berry-phase formalism within DFT + *U* [68,71,73,74]. The polarization along lattice vector $R_\mu^{(\lambda)}$ reads [15,56]

$$P_\mu^{(\lambda)} = \frac{e}{2\pi} \frac{\varphi_\mu^{(\lambda)}}{\Omega^{(\lambda)}} R_\mu^{(\lambda)}, \quad (\text{A7})$$

and the spontaneous polarization is obtained from the difference between polar and centrosymmetric phases. This approach reliably captures vacancy- and doping-induced

TABLE VII. CFPs B_{kq} (cm^{-1}) for Gd^{3+} in defect-designed PbTiO_3 , obtained from DFT (open-core 4f) and SPM approaches. Results are shown for $\text{Pb}_{1-x-\delta}\text{Gd}_x\text{TiO}_3$ (Gd at Pb site with Pb vacancy), $\text{Pb}_{1-x}\text{Gd}_x\text{TiO}_3$ (Pb-site Gd without vacancies), and $\text{PbTi}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$ (Ti-site Gd with O vacancy), with $x = 0.125$ and $\delta = 0.0625$. Symmetry lowering from C_{4v} to C_{2v} in the Pb-vacancy system leads to activation of the nonaxial CFPs (B_{22} , B_{42} , B_{62}). Benchmark values for $\text{YVO}_4\text{:Gd}^{3+}$, $\text{YPO}_4\text{:Gd}^{3+}$, and $\text{YAsO}_4\text{:Gd}^{3+}$ are included for comparison [88].

Compound	Supercell	Gd Site	Symmetry	B_{20}	B_{22}	B_{40}	B_{42}	B_{44}	B_{60}	B_{62}	B_{64}	B_{66}	Method	Ref.				
$\text{Pb}_{1-x-\delta}\text{Gd}_x\text{TiO}_3$	$2 \times 2 \times 4$	Gd1	C_{2v}	-1325.1	153.3	-627.3	-10.2	91.1	293.0	-10.4	824.4	20.8	DFT	*				
				-962.3	-68.9	-3359.1	660.7	-1583.4	167.0	133.6	1241.5	-19.8	SPM(a)	*				
				-771.1	-55.2	2693.4	529.8	-1269.6	133.7	107.0	994.3	-15.9	SPM(b ⁻)	*				
				-1154.5	-82.6	-4029.3	792.5	-1899.4	200.6	160.5	1491.5	-23.8	SPM(b ⁺)	*				
				-717.3	-81.8	-2866.7	518.3	-1527.1	104.4	107.7	979.0	-18.1	SPM(c ⁻)	*				
				-1180.9	-50.7	-3977.8	837.9	-1617.8	237.7	165.5	1591.2	-20.9	SPM(c ⁺)	*				
		Gd2		-1064.5	0.5	-259.4	0.6	-320.5	-129.9	-0.5	881.7	0.3	DFT	*				
				-1181.0	-19.5	-3186.0	19.8	-1995.0	184.1	36.2	1250.0	-28.3	SPM(a)	*				
				-946.7	-15.6	-2555.7	15.9	-1600.3	147.5	29.0	1001.8	-22.7	SPM(b ⁻)	*				
				-1417.5	-23.4	-3823.3	23.7	-2394.0	221.3	43.5	1502.8	-34.1	SPM(b ⁺)	*				
				-877.2	-13.9	-2781.3	22.1	-1815.8	114.1	48.3	992.6	-22.3	SPM(c ⁻)	*				
				-1474.2	-26.7	-3071.8	15.7	-2179.7	265.0	48.3	1592.6	-26.3	SPM(c ⁺)	*				
				$\text{Pb}_{1-x}\text{Gd}_x\text{TiO}_3$	$2 \times 2 \times 2$	Gd	C_{4v}	-968.2	0.0	-480.8	0.0	-221.1	17.6	0.0	921.5	0.0	DFT	*
								-720.3		-2838.3		-1301.8	67.0		811.5		SPM(a)	*
-576.3		-2270.7						-1041.4	53.6		649.2		SPM(b ⁻)	*				
-864.4		-3406.0						-1562.2	80.5		973.8		SPM(b ⁺)	*				
-526.6		-2568.7						-1257.4	28.2		680.7		SPM(c ⁻)	*				
-896.5		-3177.5						-1331.2	107.9		977.9		SPM(c ⁺)	*				
$\text{PbTi}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$	$2 \times 2 \times 4$	Gd1	C_{2v}	-1408.8		2645.9		2383.3	245.5		-782.8		DFT	*				
				-699.4		3624.2		3101.8	-4.3		-244.2		SPM(a)	*				
				-560.1		2904.0		2485.4	-3.5		-195.3		SPM(b ⁻)	*				
				-838.6		4344.4		3718.2	-5.2		-293.0		SPM(b ⁺)	*				
				-546.2		3676.8		3234.8	-37.0		-227.7		SPM(c ⁻)	*				
				-850.0		3584.4		3234.8	-37.0		-261.9		SPM(c ⁺)	*				
		Gd2		-3155.3		1624.7		2520.0	514.4		-333.8		DFT	*				
				-1280.8		1950.8		3048.6	65.2		-122.3		SPM(a)	*				
				-1025.8		1563.2		2442.8	52.1		-97.9		SPM(b ⁻)	*				
				-1535.9		2338.5		3654.5	78.2		-146.8		SPM(b ⁺)	*				
				-1147.5		1966.9		2888.8	78.2		-111.8		SPM(c ⁻)	*				
				-1414.1		1945.4		3217.4	53.9		-133.8		SPM(c ⁺)	*				
				$\text{YVO}_4\text{:Gd}^{3+}$	Gd	-371		316		1225	-827		-138		SPM	[88]		
						519		296		1264	-818		27			[88]		
-215		292				1484	-624		-44			[88]						

polarization changes; further details are given in the SM (Secs. SM II E and SM II L) [16].

APPENDIX B: COMPUTATIONAL METHODS

First-principles calculations were performed within DFT using the FP-APW + lo method as implemented in WIEN2k [59,60]. Exchange-correlation effects were treated within the PBE generalized-gradient approximation (GGA) [107,108] augmented by on-site Coulomb corrections in the Dudarev formalism (GGA + U_{eff}). Literature-based values $U_{\text{eff}}^{\text{Gd}} = 4.35$ eV for Gd 4f states [81] and $U_{\text{eff}}^{\text{Ti}} = 3.94$ eV for Ti 3d states [82] were adopted, ensuring a physically meaningful description of localized f and correlated d electrons. The dependence of the electronic and magnetic properties on the choice of U_{eff} was explicitly examined by varying U_{eff} over physically relevant ranges. Consistent with prior systematic benchmarks [15,83], moderate variations in U_{eff} do not alter the qualitative conclusions of this work, including the insulating versus metallic character, defect-compensation

mechanism, magnetic moments, or magnetic anisotropy. A detailed justification of the adopted U_{eff} values and a quantitative robustness analysis are provided in the SM (Sec. SM II F) [16]. Spin polarization and spin-orbit coupling were included throughout.

Structural relaxations were carried out for tetragonal $P4mm$ supercells: $2 \times 2 \times 2$ for uncompensated doping and $2 \times 2 \times 4$ for vacancy-stabilized configurations, whereas the equilibrium geometries were obtained via Birch-Murnaghan fits [113]. Motivated by studies reporting magnetism in Fe- and Gd-doped PbTiO_3 [10], both ferromagnetic (FM) and antiferromagnetic (AFM) orderings were examined. Defect formation energies were computed with $2 \times 2 \times 4$ supercells using the total-energy difference method with atomic energy corrections, following Ref. [13].

Electronic band gaps were evaluated using the modified Becke-Johnson exchange potentials TB-mBJ and JTSKTB-mBJ [48,49,54], which are known to significantly improve band-gap predictions relative to semilocal PBE-GGA and to yield values comparable to experiment for a wide range of

TABLE VIII. Magnetic response of Gd^{3+} ions obtained from CFT analysis, including CF splittings $\varepsilon_i(0)$ (meV), $\mathbf{g}$ -tensor components, and Van Vleck susceptibilities for the $^8S_{7/2}$ multiplet at distinct Gd sites (Gd1, Gd2). Results are presented for $\text{Pb}_{1-x-\delta}\text{Gd}_x\text{TiO}_3$ and $\text{PbTi}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$ using both DFT+CFT+ Δ +Zeeman+Reg. and optimized SPM(b^-)+CFT+Zeeman+Reg. schemes.

Method	DFT+CFT+ Δ +Zeem.+Reg.					SPM(b^-)+CFT+Zeem.+Reg.				
Compound	$\text{Pb}_{1-x-\delta}\text{Gd}_x\text{TiO}_3$									
i (doublet)	$\varepsilon_i(0)$ [meV]	$\mathbf{g}_{i\perp}$	$\mathbf{g}_{i\parallel}$	$\chi_{i\perp}^{vV}$	$\chi_{i\parallel}^{vV}$	$\varepsilon_i(0)$ [meV]	$\mathbf{g}_{i\perp}$	$\mathbf{g}_{i\parallel}$	$\chi_{i\perp}^{vV}$	$\chi_{i\parallel}^{vV}$
Gd1										
1	0.00	13.326	-0.359	0.3674	7.3183	0.00	13.172	2.869	0.5294	8.1409
2	0.00	5.945	0.059	2.8469	6.7008	0.00	7.171	4.433	1.9703	4.2846
3	0.04	0.036	2.268	4.0596	4.3635	0.02	3.097	6.120	1.9868	0.1921
4	0.04	-6.603	4.935	5.6728	-0.4060	0.02	-1.751	6.070	2.7860	-2.8636
5	0.11	-4.659	6.945	1.1919	-5.7118	0.06	-2.932	3.966	0.6846	-4.5604
6	0.11	-6.478	3.503	-1.1012	-6.9617	0.06	-7.466	-1.541	0.9895	-3.5353
7	0.20	-1.582	-3.406	-4.9565	-5.2972	0.11	-5.560	-7.962	-3.0541	1.6567
8	0.20	0.015	-13.946	-8.0810	-0.0058	0.11	-5.730	-13.956	-5.8926	-0.0014
Gd2										
1	0.00	12.89	0.186	0.6917	8.4845	0.00	12.845	0.104	0.7457	9.3153
2	0.00	6.606	1.743	2.2701	6.2405	0.00	6.346	2.394	2.4702	5.6903
3	0.03	2.031	4.309	2.5736	2.1647	0.03	2.377	5.139	2.3391	1.2846
4	0.03	-3.950	5.829	4.1300	-1.9575	0.03	-2.884	6.440	3.4902	-2.6774
5	0.08	-3.957	5.729	1.1530	-5.4424	0.08	-3.361	5.840	0.9332	-5.7039
6	0.08	-8.301	1.3920	1.2936	-5.6256	0.08	-7.803	0.595	1.0673	-5.1097
7	0.16	-3.028	-5.230	-4.3943	-3.8641	0.15	-4.112	-6.555	-3.8591	-2.7979
8	0.16	-2.300	-13.958	-7.7177	-0.0000	0.15	-3.408	-13.956	-7.1866	-0.0012
Compound	$\text{PbTi}_{1-x}\text{Gd}_{0.125}\text{O}_{3-\delta}$									
Gd1										
1	0.00	12.506	0.574	0.8944	5.8774	0.00	13.246	4.521	0.4767	6.6490
2	0.00	6.062	0.329	2.5348	5.9005	0.00	8.557	6.084	0.9595	3.2894
3	0.03	0.554	0.384	3.4356	5.6837	0.01	3.530	6.291	1.758	0.1041
4	0.03	-6.542	2.679	5.4104	1.8002	0.01	-2.176	4.446	3.0235	-1.7120
5	0.11	-4.019	6.094	0.48145	-4.4610	0.04	-4.43	2.03	1.6195	-3.0821
6	0.11	-7.413	4.467	-0.0731	-7.2820	0.04	-7.763	-2.256	1.3948	-2.9472
7	0.22	-1.100	-0.572	-4.7827	-7.5177	0.10	-4.389	-7.171	-3.8348	-2.2976
8	0.22	-0.049	-13.956	-7.9010	-0.0012	0.10	-6.570	-13.952	-5.3978	-0.0036
Gd2										
1	0.00	11.373	0.160	1.4305	2.8156	0.00	12.699	0.575	0.794	7.1669
2	0.00	1.551	-0.381	5.0871	3.2648	0.00	6.80	0.678	2.0957	6.8801
3	0.08	-2.046	0.777	3.8659	2.1921	0.03	1.411	2.890	3.0344	3.559
4	0.08	-8.851	-1.174	4.2826	3.9440	0.03	-5.271	4.858	4.8562	-0.8246
5	0.24	-1.328	1.795	-2.0801	1.0485	0.09	-4.210	5.991	0.9543	-5.2822
6	0.24	-0.835	-2.730	-5.6671	5.5203	0.09	-7.915	2.526	0.8596	-6.3121
7	0.48	-0.072	15.510	-3.1770	-18.7850	0.18	-1.960	-3.561	-4.7533	-5.1857
8	0.48	0.208	-13.958	-3.7418	-0.0003	0.18	-1.556	-13.955	-7.8411	-0.0016

oxide materials, including perovskites. The performance of these approaches for PbTiO_3 and related systems has been systematically benchmarked in Ref. [56]. We note that hybrid exchange-correlation functionals such as B3PW and B3LYP have been shown to reproduce experimental band gaps of ABO_3 perovskites with excellent accuracy [114]. In contrast, as is well established, semilocal functionals such as PBE-GGA tend to underestimate band gaps. In the present work, TB-mBJ-based methods provide an efficient and reliable route to accurate band-gap estimation within large defect-containing supercells, consistent with the scope of the study.

It is important to note that agreement with experiment is only physically meaningful when the calculated quantity corresponds to the experimentally measured observable. In PbTiO_3 , the reported band gap is typically an optical gap rather than a quasiparticle gap. While it is possible to tune U , the hybrid-functional mixing parameter α , or the c parameter in mBJ-based schemes to reproduce a target gap value, such tuning is only justified if it yields an optical gap consistent with experiment. In this context, TB-mBJ-based approaches provide a balanced description of the electronic structure at a computational cost compatible with large, defect-containing supercells, while avoiding *ad hoc* parameter fitting.

To determine the CFPs for Gd^{3+} , two complementary methods were employed: (i) DFT + SPM, using structural inputs and semiempirical intrinsic coefficients [46,86], and (ii) DFT + CFT, in which Bloch wave functions were projected onto maximally localized Wannier functions (via WIEN2WANNIER and WANNIER90 [26,31,87]), and the local Hamiltonian was expanded in spherical tensors to extract CFPs. Robustness was assessed through sensitivity testing of the SPM, using three specific variants—SPM(a) with nominal inputs; SPM(b $^\pm$), varying $\bar{A}_k$ by $\pm 20\%$; and SPM(c $^\pm$), varying t_k by $\pm 20\%$ —resulting in five total test cases. Effective Zeeman $\mathbf{g}$ tensors and Van Vleck susceptibilities were obtained from quadratic fits of field-induced splittings, incorporating Gd $4f$ –O $2p/2s$ hybridization with $\Delta = -0.6$ Ry [25].

This multifacet framework—spanning structural relaxation, defect energetics, electronic correlations, optical gaps, polarization, and CF modeling—provides a predictive description of how aliovalent Gd doping and intrinsic defects stabilize multifunctional behavior in PbTiO_3 . Full computational details are given in Sec. SM III and its subsections in the SM [16].

APPENDIX C: CFPs AND MAGNETIC-RESPONSE TENSORS

This Appendix provides the complete numerical datasets underlying the CF and magnetic-response analysis presented in Sec. II F. The tables below report the full sets of CFPs, CF-induced level splittings, $\mathbf{g}$ -tensor components, and Van Vleck susceptibilities obtained for all crystallographically distinct Gd^{3+} sites and defect configurations explicitly considered in this work.

The CFPs B_{kq} listed in Table VII were obtained using two complementary approaches: (i) first-principles projections of open-core Gd $4f$ states within DFT and (ii) semiempirical superposition model (SPM) calculations using multiple parametrizations. The reported values correspond to well-defined local defect motifs represented explicitly by the employed supercells.

The symmetry labels given in Table VII refer exclusively to the *local point-group symmetry* of the Gd^{3+} coordination environment for the specific defect geometry under consideration. These labels are not intended to describe the global crystallographic symmetry of the host lattice, which remains tetragonal ($P4mm$) at dilute doping levels, as discussed in the main text. The presence or absence of nonaxial CFPs ($q = 2, 6$) in the table follows directly from these local site symmetry assignments.

Benchmark CFPs for well-characterized oxide hosts (YVO_4 , YPO_4 , and YAsO_4 doped with Gd^{3+}) are included in Table VII to place the magnitudes obtained for PbTiO_3 -based systems in a broader physical context.

Table VIII summarizes the magnetic-response quantities derived from CFT, including zero-field splittings $\varepsilon_i(0)$ of the $^8S_{7/2}$ multiplet, principal components of the $\mathbf{g}$ tensor, and Van Vleck susceptibilities for each inequivalent Gd^{3+} site. Results are shown for both the fully *ab initio* DFT + CFT + Δ + Zeeman + Reg. scheme and the optimized semiempirical SPM(b $^-$) + CFT + Zeeman + Reg. approach.

The close quantitative agreement between these two schemes across all configurations demonstrates that the essential features of the magnetic anisotropy are governed by the local CF environment and are robust with respect to the computational framework used to extract the CFPs.

The datasets reported here correspond to specific local environments defined by explicit vacancy-dopant configurations within the supercell models. In experimentally relevant samples, dopants and compensating vacancies are expected to be distributed in a largely disordered manner. Such disorder does not alter the local CFPs associated with a given defect motif but leads to orientational and configurational averaging of macroscopic tensor quantities, such as susceptibilities and effective $\mathbf{g}$ tensors.

Accordingly, the CFPs and magnetic-response tensors reported in Tables VII and VIII should be viewed as transferable local building blocks for modeling magnetism in disordered Gd-doped PbTiO_3 systems.

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- [1] R. Nelmes and W. Kuhs, The crystal structure of tetragonal PbTiO_3 at room temperature and at 700 K, *Solid State Commun.* **54**, 721 (1985).
 - [2] A. Glazer and S. Mabud, Powder profile refinement of lead zirconate titanate at several temperatures. II. pure PbTiO_3 , *Acta Cryst. B* **34**, 1065 (1978).
 - [3] B. Jaffe, R. S. Roth, and S. Marzullo, Properties of piezoelectric ceramics in the solid-solution series lead titanate-lead zirconate-lead oxide: tin oxide and lead titanate-lead hafnate, *J. Res. Natl. Bur. Stand.* **55**, 239 (1955).
 - [4] D. K. Pradhan, A. K. Mishra, S. Kumari, A. Basu, M. Somayazulu, E. Gradauskaitė, R. M. Smith, J. Gardner, P. W. Turner, A. T. N'Diaye, *et al.*, Studies of multiferroic palladium perovskites, *Sci. Rep.* **9**, 1685 (2019).
 - [5] J. Liu, V. V. Laguta, K. Inzani, W. Huang, S. Das, R. Chatterjee, E. Sheridan, S. M. Griffin, A. Ardavan, and R. Ramesh, Coherent electric field manipulation of Fe^{3+} spins in PbTiO_3 , *Sci. Adv.* **7**, eabf8103 (2021).
 - [6] Y. Yan, J. E. Zhou, D. Maurya, Y. U. Wang, and S. Priya, Giant piezoelectric voltage coefficient in grain-oriented modified PbTiO_3 material, *Nat. Commun.* **7**, 13089 (2016).
 - [7] M. Kellati, S. Sayouri, N. El Moudden, M. Elaatmani, A. Kaal, and M. Taibi, Structural and dielectric properties of La-doped lead titanate ceramics, *Mater. Res. Bull.* **39**, 867 (2004).
 - [8] R. Tickoo, R. Tandon, K. Bamzai, and P. Kotru, Dielectric and piezoelectric characteristics of samarium modified lead titanate ceramics, *Mater. Sci. Eng. B* **103**, 145 (2003).
 - [9] S. C. Panigrahi, P. R. Das, R. Padhee, and R. N. P. Choudhary, Effect of Gd on dielectric and piezoelectric properties of lead zirconate titanate ferroelectric ceramics, *Ferroelectrics* **524**, 14 (2018).

- [10] D. P. Dutta, B. P. Mandal, E. Abdelhamid, R. Naik, and A. K. Tyagi, Enhanced magneto-dielectric coupling in multiferroic Fe and Gd codoped PbTiO_3 nanorods synthesized via microwave assisted technique, *Dalton Trans.* **44**, 11388 (2015).
- [11] E. Erdem, P. Jakes, S. K. S. Parashar, K. Kiraz, M. Somer, A. Rüdiger, and R.-A. Eichel, Defect structure in aliovalently-doped and isovalently-substituted PbTiO_3 nano-powders, *J. Phys.: Condens. Matter* **22**, 345901 (2010).
- [12] A. Nayak, S. Patri, B. Behera, S. Sahoo, and S. Anwar, Rare earth doping driven multifunctional properties of PbTiO_3 derivatives, *Mater. Chem. Phys.* **322**, 129573 (2024).
- [13] M. Acikgoz, L. Mollabashi, S. Rahimi, S. Jalali-Asadabadi, and C. Rudowicz, DFT computations combined with semiempirical modeling of variations with temperature of spectroscopic and magnetic properties of Gd^{3+} -doped PbTiO_3 , *Phys. Chem. Chem. Phys.* **25**, 3986 (2023).
- [14] G. Shirane and S. Hoshino, On the phase transition in lead titanate, *J. Phys. Soc. Jpn.* **6**, 265 (1951).
- [15] S. Rahimi, S. Jalali-Asadabadi, P. Blaha, and F. Jalali-Asadabadi, Nonzero spontaneous electric polarization in metals: novel predictive methods and applications, *Sci. Rep.* **14**, 672 (2024).
- [16] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/f9s8-1zxn> for detailed theoretical formulations and computational methodologies, including DFT+U protocols, defect energetics, Berry-phase polarization calculations, crystal-field modeling (DFT+CFT and SPM+CFT), temperature-dependent magnetic susceptibility analysis, optical band-gap evaluation (TB-mBJ and JTSKTB-mBJ), QTAIM charge-density analysis, and additional figures and tables supporting the current paper.
- [17] S. Hüfner, *Optical Spectra of Transparent Rare Earth Compounds*, 1st ed. (Academic Press, New York, 1978).
- [18] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, International series of monographs on physics (Clarendon Press, Oxford, 1970).
- [19] B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience Publishers, New York, 1965).
- [20] C. Rudowicz, Transformation relations for the conventional O_kq and normalised O'_kq Stevens operator equivalents with $k = 1$ to 6 and $-k \leq q \leq k$, *J. Phys. C: Solid State Phys.* **18**, 1415 (1985).
- [21] C. Rudowicz and M. Karbowiak, Disentangling intricate web of interrelated notions at the interface between the physical (crystal field) Hamiltonians and the effective (spin) Hamiltonians, *Coord. Chem. Rev.* **287**, 28 (2015).
- [22] C. Rudowicz, P. Gnutek, and M. Açıkgöz, Superposition model in electron magnetic resonance spectroscopy – a primer for experimentalists with illustrative applications and literature database, *Appl. Spectrosc. Rev.* **54**, 673 (2019).
- [23] L. Mollabashi and S. Jalali-Asadabadi, Crystal fields of lithium rare-earth tetrafluorides and multiplet splitting of the +3 rare-earth ions, *Phys. Rev. B* **102**, 045120 (2020).
- [24] L. Mollabashi, E. Sadeghi Kelishadi, and S. Jalali-Asadabadi, Crystal field and Ce^{3+} ion energy levels of CeCl_3 compound, *Iran. J. Phys. Res.* **18**, 105 (2019).
- [25] L. Mollabashi, S. Jalali-Asadabadi, C. Rudowicz, M. Acikgoz, Z. Ghasemi-Dorcheh, R. Ebrahimi-Jaberi, M. Jalali-Asadabadi, S. Rahimi, and F. Jalali-Asadabadi, Numerical study of the temperature-dependent magnetization and susceptibility of Tm^{3+} in LiTmF_4 , *Phys. Rev. B* **110**, 054440 (2024).
- [26] P. Novák, K. Knížek, and J. Kuneš, Crystal field parameters with Wannier functions: Application to rare-earth aluminates, *Phys. Rev. B* **87**, 205139 (2013).
- [27] S. J. Asadabadi, S. Cottenier, H. Akbarzadeh, R. Saki, and M. Rots, Valency of rare earths in $R\text{In}_3$ and $R\text{Sn}_3$: *Ab initio* analysis of electric-field gradients, *Phys. Rev. B* **66**, 195103 (2002).
- [28] S. Asadabadi and H. Akbarzadeh, Density functional approach to study structural properties and electric field gradients in rare earth materials, *Phys. B* **349**, 76 (2004).
- [29] S. Jalali Asadabadi, Electronic structure and electric-field gradient analysis in CeIn_3 , *Phys. Rev. B* **75**, 205130 (2007).
- [30] J. Kuneš, R. Arita, P. Wissgott, A. Toschi, H. Ikeda, and K. Held, Wien2wannier: From linearized augmented plane waves to maximally localized Wannier functions, *Comput. Phys. Commun.* **181**, 1888 (2010).
- [31] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Wannier90: A tool for obtaining maximally-localised Wannier functions, *Comput. Phys. Commun.* **178**, 685 (2008).
- [32] A. A. Mostofi, J. R. Yates, G. Pizzi, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, An updated version of Wannier90: A tool for obtaining maximally-localised Wannier functions, *Comput. Phys. Commun.* **185**, 2309 (2014).
- [33] N. Marzari and D. Vanderbilt, Maximally localized generalized Wannier functions for composite energy bands, *Phys. Rev. B* **56**, 12847 (1997).
- [34] I. Souza, N. Marzari, and D. Vanderbilt, Maximally localized Wannier functions for entangled energy bands, *Phys. Rev. B* **65**, 035109 (2001).
- [35] D. J. Newman and W. Urban, Interpretation of *S*-state ion E.P.R. spectra, *Adv. Phys.* **24**, 793 (1975).
- [36] D. J. Newman and B. Ng, The superposition model of crystal fields, *Rep. Prog. Phys.* **52**, 699 (1989).
- [37] *Crystal Field Handbook*, edited by D. J. Newman and B. Ng (Cambridge University Press, Cambridge, 2000).
- [38] M. Andrut, M. Wildner, and C. Z. Rudowicz, Optical absorption spectroscopy in geosciences: Part II: Quantitative aspects of crystal fields, in *Spectroscopic Methods in Mineralogy, EMU Notes in Mineralogy*, Vol. 6 (Mineralogical Society of Great Britain and Ireland, Twickenham, 2004), pp. 93–144.
- [39] K. W. H. Stevens, Matrix elements and operator equivalents connected with the magnetic properties of rare earth ions, *Proc. Phys. Soc. A* **65**, 209 (1952).
- [40] M. T. Hutchings, *Point-Charge Calculations of Energy Levels of Magnetic Ions in Crystalline Electric Fields*, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1964), Vol. 16, pp. 227–273.
- [41] J. Jensen and A. R. Mackintosh, *Rare Earth Magnetism: Structures and Excitations*, International Series of Monographs on Physics (Clarendon Press, Oxford, 1991).
- [42] J. Mulak and Z. Gajek, *The Effective Crystal Field Potential* (Elsevier, New York, 2000).
- [43] Y. Wan-Lun and Z. Min-Guang, Spin-Hamiltonian parameters of f -state ions, *Phys. Rev. B* **37**, 9254 (1988).
- [44] M. Açıkgöz, R. Kripal, M. G. Misra, A. K. Yadav, P. Gnutek, and C. Rudowicz, Theoretical analysis of crystal field parameters and zero field splitting parameters for Mn^{2+}

- ions in tetramethylammonium tetrachlorozincate (TMATC-Zn), *Polyhedron* **235**, 116341 (2023).
- [45] A. Biswas, S. Sarkar, Y. M. Jana, D. Swarnakar, S. Nandi, C. Rudowicz, M. Açıkgöz, and N. M. Avram, Analysis of crystal-field effect on luminescence spectra of Mn^{4+} ($3d^3$) ion-doped double perovskite $\text{La}_2\text{ZnTiO}_6$ phosphor by semiempirical computations: exchange charge model and superposition model, *J. Mater. Chem. C* **10**, 4355 (2022).
- [46] W.-Q. Yang and W.-C. Zheng, Spin-Hamiltonian parameters of Gd^{3+} ion in the room temperature tetragonal phase of BaTiO_3 , *Z. Naturforsch. A* **69**, 606 (2014).
- [47] C. Görrler-Walrand and K. Binnemans, Optical spectroscopy and electronic structure of rare-earth ions in crystals, in *Handbook on the Physics and Chemistry of Rare Earth*, edited by K. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1996), Vol. 23.
- [48] F. Tran and P. Blaha, Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential, *Phys. Rev. Lett.* **102**, 226401 (2009).
- [49] D. Koller, F. Tran, and P. Blaha, Merits and limits of the modified Becke-Johnson exchange potential, *Phys. Rev. B* **83**, 195134 (2011).
- [50] M. Yazdanmehr, S. J. Asadabadi, A. Nourmohammadi, M. Ghasemzadeh, and M. Rezvanian, Electronic structure and bandgap of Al_2O_3 compound using mBJ exchange potential, *Nanoscale Res. Lett.* **7**, 488 (2012).
- [51] S. Jalali-Asadabadi, E. Ghasemikhah, T. Ouahrani, B. Nourozi, M. Bayat-Bayatani, S. Javanbakht, H. A. R. Aliabad, I. Ahmad, J. Nematollahi, and M. Yazdani-Kachoei, Electronic structure of crystalline buckyballs: fcc- C_{60} , *J. Electron. Mater.* **45**, 339 (2016).
- [52] M. Yazdanmehr, S. Jalali-Asadabadi, J. Nematollahi, A. Nourmohammadi, and I. Ahmad, Predictions of bandgap and subbands of $\gamma - \text{Al}_2\text{O}_3$ in presence of intrinsic point defects by DFT+TB-mBJ, *Comput. Condens. Matter* **19**, e00379 (2019).
- [53] G. Rehman, M. Shafiq, Saifullah, R. Ahmad, S. Jalali-Asadabadi, M. Maqbool, I. Khan, H. Rahnamaye-Aliabad, and I. Ahmad, Electronic band structures of the highly desirable III–V semiconductors: TB-mBJ DFT Studies, *J. Electron. Mater.* **45**, 3314 (2016).
- [54] R. A. Jishi, O. B. Ta, and A. A. Sharif, Modeling of lead halide perovskites for photovoltaic applications, *J. Phys. Chem. C* **118**, 28344 (2014).
- [55] J. Tauc, R. Grigorovici, and A. Vancu, Optical properties and electronic structure of amorphous germanium, *Physica Status Solidi (b)* **15**, 627 (1966).
- [56] S. Rahimi, R. Ebrahimi-Jaberi, F. Jalali-Asadabadi, L. Mollabashi, and S. Jalali-Asadabadi, Influence of (Ba,F) multidoping on structural, magnetic, optical, and electrical properties as well as performance enhancement of multiferroic BiFeO_3 , *Phys. Rev. B* **106**, 115205 (2022).
- [57] R. F. W. Bader, A quantum theory of molecular structure and its applications, *Chem. Rev.* **91**, 893 (1991).
- [58] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, International Series of Monographs on Chemistry (Clarendon Press, Oxford, 1994).
- [59] E. Sjöstedt, L. Nordström, and D. Singh, An alternative way of linearizing the augmented plane-wave method, *Solid State Commun.* **114**, 15 (2000).
- [60] G. K. Madsen, P. Blaha, K. Schwarz, E. Sjöstedt, and L. Nordström, Efficient linearization of the augmented plane-wave method, *Phys. Rev. B* **64**, 195134 (2001).
- [61] K. Schwarz and P. Blaha, Solid state calculations using WIEN2K, *Comput. Mater. Sci.* **28**, 259 (2003).
- [62] P. Blaha, K. Schwarz, F. Tran, R. Laskowski, G. K. H. Madsen, and L. D. Marks, WIEN2K: An APW+lo program for calculating the properties of solids, *J. Chem. Phys.* **152**, 074101 (2020).
- [63] P. Blaha, K. Schwarz, G. K. Madsen, D. Kvasnicka, J. Luitz, R. Laskowski, F. Tran, and L. D. Marks, WIEN2k, in *An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties*, edited by Prof. Dr. Karlheinz Schwarz (Vienna University of Technology, Institute of Materials Chemistry, Getreidemarkt 9/165-TC, A-1060 Vienna, Austria, 2023).
- [64] A. O. de-la Roza, M. Blanco, A. M. Pendás, and V. Luaña, Critic: a new program for the topological analysis of solid-state electron densities, *Comput. Phys. Commun.* **180**, 157 (2009).
- [65] A. O. de-la Roza, E. R. Johnson, and V. Luaña, Critic2: A program for real-space analysis of quantum chemical interactions in solids, *Comput. Phys. Commun.* **185**, 1007 (2014).
- [66] M. Yazdani-Kachoei and S. Jalali-Asadabadi, Topological analysis of electron density in half-Heusler ZrXB_i ($M = \text{Co}, \text{Rh}$) compounds: A density functional theory study accompanied by Bader's quantum theory of atoms in molecules, *J. Alloys Compd.* **828**, 154287 (2020).
- [67] M. Yazdani-Kachoei, S. Jalali-Asadabadi, and N. Arianmehr, Topological analysis of CeMIn_5 ($M = \text{Co}, \text{Rh}$) electron charge densities, *Comput. Mater. Sci.* **164**, 205 (2019).
- [68] M. V. Berry, Classical adiabatic angles and quantal adiabatic phase, *J. Phys. A: Math. Gen.* **18**, 15 (1985).
- [69] D. Vanderbilt, Berry-phase theory of proper piezoelectric response, *J. Phys. Chem. Solids* **61**, 147 (2000).
- [70] M. V. Berry, Quantal phase factors accompanying adiabatic changes, *Proc. R. Soc. Lond. Ser. A* **392**, 45 (1984).
- [71] D. Xiao, M.-C. Chang, and Q. Niu, Berry phase effects on electronic properties, *Rev. Mod. Phys.* **82**, 1959 (2010).
- [72] S. Ahmed, J. Kivinen, B. Zaporzan, L. Curiel, S. Pichardo, and O. Rubel, BerryPI: A software for studying polarization of crystalline solids with WIEN2k density functional all-electron package, *Comput. Phys. Commun.* **184**, 647 (2013).
- [73] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Band theory and Mott insulators: Hubbard U instead of Stoner I , *Phys. Rev. B* **44**, 943 (1991).
- [74] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, First-principles calculations of the electronic structure and spectra of strongly correlated systems: the LDA + U method, *J. Phys.: Condens. Matter* **9**, 767 (1997).
- [75] F. Ge, W. Wu, X. Wang, H. Wang, Y. Dai, H. Wang, and J. Shen, The first-principle calculation of structures and defect energies in tetragonal PbTiO_3 , *Physica B* **404**, 3814 (2009).
- [76] S. Piskunov, E. Heifets, R. Eglitis, and G. Borstel, Bulk properties and electronic structure of SrTiO_3 , BaTiO_3 , PbTiO_3 perovskites: an *ab initio* HF/DFT study, *Comput. Mater. Sci.* **29**, 165 (2004).
- [77] C. H. Peng, J.-F. Chang, and S. B. Desu, Optical properties of PZT, PLZT, and PNZT thin films, *MRS Online Proc. Libr.* **243**, 21 (1991).

- [78] R. Thomas and D. C. Dube, Structural, electrical and optical properties of sol–gel processed lead titanate thin films, *Jpn. J. Appl. Phys.* **36**, 7337 (1997).
- [79] V. Železný, D. Chvostová, D. Šimek, F. Máca, J. Mašek, N. Setter, and Y. H. Huang, The variation of PbTiO_3 bandgap at ferroelectric phase transition, *J. Phys.: Condens. Matter* **28**, 025501 (2015).
- [80] M. K. Gerges, M. Mostafa, and G. M. Rashwan, Structural, optical and electrical properties of PbTiO_3 nanoparticles prepared by Sol-Gel method, *International Journal of Latest Research in Engineering and Technology (IJLRET)* **2**, 42 (2016).
- [81] L. Bjaalie, A. Verma, B. Himmetoglu, A. Janotti, S. Raghavan, V. Protasenko, E. Steenbergen, D. Jena, S. Stemmer, and C. G. Van de Walle, Determination of the Mott-Hubbard gap in GdTiO_3 , *Phys. Rev. B* **92**, 085111 (2015).
- [82] T. Shimada, T. Xu, Y. Araki, J. Wang, and T. Kitamura, Multiferroic dislocations in ferroelectric PbTiO_3 , *Nano Lett.* **17**, 2674 (2017).
- [83] R. Ebrahimi-Jaberi and S. Jalali-Asadabadi, Elasticity and stability of GdAl_2 under pressure and temperature investigated using DFT+AI, *Sci. Rep.* **15**, 15573 (2025).
- [84] H. J. Monkhorst and J. D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B* **13**, 5188 (1976).
- [85] T. Shimada, Y. Uratani, and T. Kitamura, Emergence of ferromagnetism at a vacancy on a non-magnetic ferroelectric PbTiO_3 surface: A first-principles study, *Acta Mater.* **60**, 6322 (2012).
- [86] W.-Q. Yang, W.-C. Zheng, and H.-G. Liu, Spin-Hamiltonian parameters and local rotational order parameters for Gd^{3+} ion in the tetragonal phase of SrTiO_3 crystal, *Phys. B* **406**, 3450 (2011).
- [87] S. Edvardsson and D. Åberg, An atomic program for energy levels of equivalent electrons: lanthanides and actinides, *Comput. Phys. Commun.* **133**, 396 (2001).
- [88] W.-Q. Yang, Y. Lin, W. Huang, and H.-Z. Zeng, Investigations of the spin-Hamiltonian parameters and defect structures for Gd^{3+} ions in YMO_4 ($M = \text{V, P, As}$) crystals, *Phys. B* **407**, 1268 (2012).
- [89] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA + U study, *Phys. Rev. B* **57**, 1505 (1998).
- [90] A. M. Pikalov, A. V. Dorofeenko, and Y. E. Lozovik, Dispersion relations for plasmons in complex-shaped nanoparticle chains, *Phys. Rev. B* **98**, 085134 (2018).
- [91] D. Goldfarb, Gd_3^+ spin labeling for distance measurements by pulse EPR spectroscopy, *Phys. Chem. Chem. Phys.* **16**, 9685 (2014).
- [92] C. Rudowicz, M. Açıkgöz, and M. Karbowiak, Low symmetry aspects in electron magnetic resonance (EMR) and optical spectroscopy of coordination compounds of transition ions: Crucial notions and issues, literature survey and database, *Coord. Chem. Rev.* **512**, 215865 (2024).
- [93] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, 1932).
- [94] C. Penny, A. R. Muxworthy, and K. Fabian, Mean-field modeling of magnetic nanoparticles: The effect of particle size and shape on the Curie temperature, *Phys. Rev. B* **99**, 174414 (2019).
- [95] J. Y. Zhang, C. A. Jackson, S. Raghavan, J. Hwang, and S. Stemmer, Magnetism and local structure in low-dimensional Mott insulating GdTiO_3 , *Phys. Rev. B* **88**, 121104(R) (2013).
- [96] A. C. Komarek, H. Roth, M. Cwik, W.-D. Stein, J. Baier, M. Kriener, F. Bourée, T. Lorenz, and M. Braden, Magnetoelastic coupling in RTiO_3 ($R = \text{La, Nd, Sm, Gd, Y}$) investigated with diffraction techniques and thermal expansion measurements, *Phys. Rev. B* **75**, 224402 (2007).
- [97] D. S. Ellis, H. Uchiyama, S. Tsutsui, K. Sugimoto, K. Kato, D. Ishikawa, and A. Q. R. Baron, Phonon softening and dispersion in EuTiO_3 , *Phys. Rev. B* **86**, 220301(R) (2012).
- [98] I. E. Dzyaloshinskii, Thermodynamic theory of “weak” ferromagnetism in antiferromagnetic substances, *Sov. Phys. JETP.* **5**, 1259 (1957) [*Zh. Eksp. Teor. Fiz.* **32**, 1547 (1957)].
- [99] T. Moriya, New mechanism of anisotropic superexchange interaction, *Phys. Rev. Lett.* **4**, 228 (1960).
- [100] T. Moriya, Anisotropic superexchange interaction and weak ferromagnetism, *Phys. Rev.* **120**, 91 (1960).
- [101] M. Heide, G. Bihlmayer, and S. Blügel, Dzyaloshinskii-Moriya interaction accounting for the orientation of magnetic domains in ultrathin films: $\text{Fe/W}(110)$, *Phys. Rev. B* **78**, 140403(R) (2008).
- [102] W. S. Ham, A.-M. Pradipto, K. Yakushiji, K. Kim, S. H. Rhim, K. Nakamura, Y. Shiota, S. Kim, and T. Ono, Dzyaloshinskii-Moriya interaction in noncentrosymmetric superlattices, *npj Comput. Mater.* **7**, 129 (2021).
- [103] W. Raja, T. G. Allen, A. A. Said, O. Alharbi, E. Aydin, M. D. Bastiani, and S. D. Wolf, Temperature-dependent optical modeling of perovskite solar cells, *J. Phys. Chem. C* **126**, 14366 (2022).
- [104] I. Grinberg and A. M. Rappe, Nonmonotonic T_C trends in bi-based ferroelectric perovskite solid solutions, *Phys. Rev. Lett.* **98**, 037603 (2007).
- [105] I. Tomeno, J. A. Fernandez-Baca, K. J. Marty, K. Oka, and Y. Tsunoda, Simultaneous softening of acoustic and optical modes in cubic PbTiO_3 , *Phys. Rev. B* **86**, 134306 (2012).
- [106] S. Jalali-Asadbadi, Supplementary Dataset and Computational Results Supporting “Crystal field induced defect compensation in Gd-doped PbTiO preserving ferroelectricity and felectron magnetism together with finite-temperature multifunctionality”, figshare, Dataset, <https://doi.org/10.6084/m9.figshare.30488156.v2> containing optimized crystal structures, total and projected electronic densities of states, band structures, optical response data, magnetic moments, defect formation energies, and raw numerical outputs underlying the figures and analyses presented in the current paper.
- [107] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136**, B864 (1964).
- [108] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* **140**, A1133 (1965).
- [109] D. Marcinkowski, M. Fik-Jaskółka, A. Gorczyński, V. Patroniak, M. Kubicki, I. Stefaniuk, T. Ślusarski, M. Açıkgöz, D. Piwowarska, P. Gnutek, M. Korabik, M. Karbowiak, and C. Rudowicz, Critical evaluation of am-

- biguities in computational modeling of zero-field splitting parameters – case study: trigonal and triclinic dinuclear Gd^{3+} complexes, *J. Magn. Magn. Mater.* **633**, 173546 (2025).
- [110] C. Rudowicz and L. Kowalewski, Magnetocrystalline anisotropy due to $3d^n$ ions with spin $S = 2$ in magnetic oxides, *Physica B+C* **80**, 517 (1975).
- [111] C. Rudowicz, Magnetocrystalline anisotropy of Fe^{2+} ion in silicon- or germanium-substituted yttrium iron garnet at zero temperature, *J. Appl. Phys.* **53**, 593 (1982).
- [112] C. Rudowicz, A method for determination of higher-order magnetic anisotropy constants — importance of the cubic k_3 and k_4 for certain energy-level models, *J. Magn. Magn. Mater.* **30**, 285 (1983).
- [113] F. Birch, Finite elastic strain of cubic crystals, *Phys. Rev.* **71**, 809 (1947).
- [114] R. I. Eglitis and R. Jia, Review of systematic tendencies in (001), (011) and (111) surfaces using B3PW as well as B3LYP computations of BaTiO_3 , CaTiO_3 , PbTiO_3 , SrTiO_3 , BaZrO_3 , CaZrO_3 , PbZrO_3 and SrZrO_3 perovskites, *Materials* **16**, 7623 (2023).