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A Review on the Effects of Fe and Mg Doping on the Properties of ZnO Nanomaterials: A DFT Perspective

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ABSTRACT
Wurtzite zinc oxide is a reference wide-band-gap oxide for optoelectronics, yet density functional studies of its cation substitution remain fragmented and contradictory. This review critically synthesises first-principles results on Fe- and Mg-doped ZnO, two substituents of opposing chemistry: Fe, an open-shell 3d ion introducing localised spins, and Mg, a closed-shell cation whose effect is band-edge tuning. Doped-system claims are benchmarked against polymorph-resolved host calculations: GGA-PBE places the wurtzite, zinc-blende, and rocksalt gaps at 0.749, 0.637, and 0.817 eV against the experimental 3.37 eV, GGA+U raises them to 1.12, 1.00, and 1.11 eV, and hybrid functionals with the mBJ potential restore quantitative agreement for the tetrahedral phases. Against this baseline, Fe substitution yields a non-monotonic optical gap — Burstein–Moss widening at low concentration giving way to sp–d exchange narrowing at higher content and total magnetisations rising only weakly from 4.12 to 4.25 μB per supercell between 3 and 6 at% Fe, well below the 2 μB expected per added Fe atom. The ferromagnetism literature is coherently explained by bound magnetic polarons; intrinsic bulk-lattice room-temperature ferromagnetism remains unsupported. Mg widens the direct gap predictably, DFT+U experiment from 3.37 to 3.57 eV up to 8.33% Mg, before the wurtzite-to-rocksalt transition caps single-phase solubility near 40 at% Mg and limits the gap to about 4.3 eV. The exchange-correlation choice, rather than the dopant alone, governs most reported trends; finite-temperature, disorder, and self-consistent-U treatments remain the decisive open frontiers.

Keywords: Density Functional Theory; Zinc Oxide; Fe Doping; Mg Doping; Dilute Magnetic Semiconductors; Band-Gap; Optoelectronics

INTRODUCTION

Zinc oxide occupies a peculiar position in semiconductor physics. Its room-temperature direct band gap of 3.37 eV, together with a 60 meV exciton binding energy more than twice that of GaN (Ginley, 2010), has sustained a long candidacy for short-wavelength optoelectronics, transparent conducting oxide layers, and ultraviolet emitters. Structurally, ZnO crystallises in three well-known polymorphs, of which the wurtzite phase is the most thermodynamically stable. Beyond conventional optoelectronics, the community's interest was subsequently extended by the pursuit of reproducible p-type doping and the experimental search for room-temperature ferromagnetism in transition-metal-doped ZnO (Alshammari et al., 2023; Bhardwaj et al., 2024).

Two motivations drive the present review. First, Fe and Mg occupy near-opposite corners of substituent chemistry. Fe is a 3d transition metal whose 3d states straddle the band gap of ZnO and whose magnetic moment arises from interactions within the system (Chithira et al., 2021; Singh et al., 2025). Mg is a closed-shell s^2 cation with a simpler electronic configuration than Zn^{2+}, turning off the tendency of off-centering displacement (Huang et al., 2022). Second, the body of DFT work on these two systems has grown wide enough to be usefully contradictory: claims of narrow-gap photocatalytic Fe:ZnO coexist with reports of ferromagnetism potentially associated with Cu co-doping (Shim et al., 2005; Singh et al., 2025). At the same time, Mg doping is often described as a textbook band-gap widener (Etacheri et al., 2012) or as a structural destabiliser when a wurtzite-to-rocksalt transition intervenes (Kourchid et al., 2026). A focused DFT review that maps these contradictions has been missing.

We restrict this review to works traceable to the surveyed literature archive: experimental–computational hybrids on Fe:ZnO pellets and films, plane-wave supercell studies on substitutional Mg, KKR-CPA and hybrid-DFT studies of $Zn_{1-x}Mg_xO$ alloys, full-potential all-electron benchmarks of pristine ZnO across its three well-known polymorphs, and quantum-Monte-Carlo reference data. Methodological cross-comparisons are anchored to polymorph-resolved benchmarks of wurtzite, zinc-blende, and rocksalt ZnO (Darma et al., 2015).

MATERIALS AND METHODS

Early first-principles work showed that LDA and GGA-PBE substantially underestimate the ZnO band gap and place the Zn 3d states at too-shallow binding energies (Makkar & Ghosh, 2021). The error has been related to O 2p–Zn 3d repulsion and hybridisation (Colonna et al., 2022), and it is on this basis that ZnO is regarded as the textbook example of exchange-correlation limitations in oxides (Lambert & O'Regan, 2023). The lesson extends well beyond ZnO: doped wide-band-gap oxides as a class remain notoriously sensitive to the exchange-correlation treatment, as the rational design of metal-doped ZrO2 continues to demonstrate (Zhang et al., 2024).

A critical first observation, easy to overlook when absorbed in doped-system results, is that "the ZnO band gap" is not a single number. It is a function of both the polymorph and the

functional. Across the three well-known phases of ZnO itself, the full-potential and plane-wave literature converges on a consistent picture: GGA-PBE gives 0.78 eV for wurtzite ZnO (Alharshan et al., 2023) and 0.749 eV, 0.637 eV, and 0.817 eV for wurtzite, zinc-blende, and rocksalt ZnO (Darma et al., 2015); the Engel–Vosko GGA places these gaps near 1.46 eV (zinc-blende) and 1.47 eV (rocksalt, indirect) (Charifi et al., 2007); the Haq et al. (2013) FP-LAPW work demonstrates that mBJ corrections improve the gap substantially in wurtzite and zinc-blende but overestimate it in the rocksalt phase. These polymorph-resolved numbers set the scale against which any doped-system claim should be benchmarked. Comparing doped ZnO band gaps to a perovskite-structured $MgZnO_3$ reference, where Zn is octahedrally coordinated by oxygen, introduces a structural difference that should be accounted for (Lawati et al., 2023).

Hubbard U Corrections

The DFT+U family is a widely used method to nudge the Zn 3d states (and, for doped systems, the Fe 3d states) closer to their experimental binding energies (Kovalenko et al., 2021),(Singh et al., 2025). Two procedural traditions exist. The first, dominant in the doped-ZnO literature, takes U empirically: scan a small set of U values, pick the one that reproduces the experimental band gap, lattice constant, or Zn 3d binding energy of pristine ZnO, then apply it unchanged to the doped supercell (Achehboune et al., 2021),(Leon et al., 2024). The second tradition treats U as a self-consistent response function of the system. The Cococcioni & Gironcoli (2005) linear-response formalism derives the effective U from the difference between bare and screened inverse susceptibilities of atomic occupations under a localised perturbation. The Timrov et al. (2021) extension casts the same linear response into density-functional perturbation theory, reducing the cost and improving numerical accuracy while remaining entirely *ab initio*. The Quantum ESPRESSO implementation described by Giannozzi et al. (2017) formalised this approach for production use. The polymorph-resolved data of Darma et al. (2015), GGA+U band gaps of 1.12 eV, 1.00 eV, and 1.11 eV for wurtzite, zinc-blende, and rocksalt ZnO, which provide the most direct benchmark for the effect of U on the same host material across phases. The surveyed Mg:ZnO and Fe:ZnO results should therefore be read as approximate rather than quantitatively predictive wherever the dopant orbital environment differs markedly from the host.

Hybrid Functionals

For systems where DFT+U is unsatisfying, hybrid functionals mixing exact Hartree–Fock exchange offer a more rigorous, if more expensive, route. HSE defect studies tune the mixing parameter α to 0.375, reproducing ZnO band gaps between 3.4 eV and 3.44 eV and lattice constants a = 3.24 Å, c = 5.19 Å (Frodason et al., 2018). The sX functional is reported to estimate the ZnO band gap more accurately than conventional functionals (Makkar & Ghosh, 2021). A survey of standard exchange-correlation (XC) functionals for ZnO and document that LDA and GGA-PBE show a calculated error near 76% on the band gap, while PBE0, HSE06, and sX recover the experimental value more accurately (Makkar & Ghosh, 2021). The Leon et al. (2024) comparison is the cleanest cross-check for our system: PBE0 with α = 0.22 reproduces the experimental room-temperature band gap, while PBE+U values of U_O = 7.5 eV and U_{Zn} = 9.5 eV simultaneously fix the Zn 3d binding energy and the band gap. For the polymorph series, the modified Becke–Johnson (mBJ) potential corrections yield wurtzite and zinc-blende ZnO gaps in good agreement with experiment but overestimate the rocksalt band gap (Haq et al., 2013), so even a hybrid-functional claim about "the ZnO band gap" remains phase-dependent. For doped systems, most defect papers quote a tuned α, commonly chosen to reproduce the experimental band gap (Muechler et al., 2022).

Supercells, Pseudopotentials, Basis Sets

Most contemporary doped-ZnO studies use 72-atom (3×3×2) (Ciechan & Bogusławski, 2021) or 192-atom (Wickramaratne & Lyons, 2024) supercells. The Singh et al. (2025) Fe-doping supercells are 2×2×4 and 2×2×2 (3.125% and 6.25% Fe), built from plane-wave ultrasoft pseudopotentials with a 410 eV cutoff and a charge-density cutoff nine times larger.

Observations on Method

The diagnostic of the ZnO band gap's sensitivity to exchange-correlation (XC) and phase is now well established: for pristine wurtzite ZnO across one consistent benchmark set, 0.78 eV, 0.68 eV, 1.20 eV (m-GGA RSCAN), 1.98 eV (Alharshan et al., 2023). The Darma et al. (2015) comparison extends across all three ZnO polymorphs: bare GGA gives 0.749 eV, 0.637 eV, and 0.817 eV; GGA+U raises these to 1.12 eV, 1.00 eV, and 1.11 eV. The Charifi et al. (2007) comparison places the B3 band gap near 1.46 eV and the B1 band gap near 1.47 eV (the latter indirect). The Haq et al. (2013) mBJ benchmark improves the wurtzite and zinc-blende band gaps substantially but overcorrects the rocksalt band gap. Conclusions drawn from GGA-PBE alone on a band gap sensitive property such as Fe 3d localisation remain, by honest accounting, qualitative.

Pristine ZnO as the Computational Baseline

A short pivot to pristine ZnO is warranted because every result on doped ZnO inherits an error from the host calculation. Wurtzite ZnO has a = 3.25 Å and c = 5.21 Å under standard experimental conditions (Leon et al., 2024), and lattice parameters are slightly modified under LDA or GGA-PBE optimisation (Zheng et al., 2021). The conduction-band minimum (CBM) is dominated by Zn 4s and O 2s components; the valence-band maximum (VBM) is dominated by O 2p with a minor contribution from Zn 3d (Laughon et al., 2022); the Zn 3d semicore states sit around −7.5 eV below the VBM (Leon et al., 2024). Pure wurtzite ZnO has a direct Γ to Γ band gap of 3.37 eV at room temperature and an experimental exciton binding energy of 60 meV (Alshammari et al., 2023),(Makkar & Ghosh, 2021), placing it close to the Ultraviolet–visible (UV–vis) spectroscopy boundary with unusually strong room-temperature excitonic effects.

Across the three well-known polymorphs, the same Zn–O bonding gives rise to a direct band gaps in the B4 and B3 phases and an indirect band gap in the B1 phase (Darma et al., 2015). The polymorph-dependent character of the band gap has direct consequences for dopant modelling: any Fe or Mg study that compares to "the ZnO band gap" must specify which polymorph the comparison refers to. The ZnO–$MgZnO_3$ perovskite has a different crystal structure than the traditional wurtzite, zinc-blende, and rock-salt ZnO polymorphs (Lawati et al., 2023).

Fe-Doped ZnO

Site Preference and Defect Chemistry

Substitutional Fe on a Zn site is a recognised defect geometry in Fe-doped ZnO (Ali et al., 2023). X-ray photoelectron spectroscopy (XPS) on dilute Fe samples indicates a

progressive $Fe^{2+} \rightarrow Fe^{3+}$ oxidation as Fe content increases, while extended X-ray absorption fine structure spectroscopy (EXAFS) confirms a majority +3 state for bulk Fe in highly doped samples with residual +2 surface populations (Chithira et al., 2021).

Magnetic Moments, Scaling, and Exchange

The Singh et al. supercell study reports total magnetisations of 0, 4.12, and 4.25 Bohr-magnetons per cell for pristine ZnO, 3 % Fe, and 6 % Fe, respectively (Singh et al., 2025). The increment from 4.12 μB at 3.125% Fe to 4.25 μB at 6.25% Fe is far smaller than the nominal 2 μB per additional Fe atom that a non-interacting picture would predict,

Band Gap Behaviour: Non-monotonic and Concentration-Dependent

The widely repeated claim that Fe doping of ZnO "consistently reduces the band gap" does not survive a careful look at the experimental literature. Experimental studies track the optical gap across varying Fe concentrations and identify a non-monotonic response in which band-edge engineering depends on which side of the threshold the sample sits. Mihalache et al. (2023) report a blue shift and broadening of the ultraviolet (UV) emission in dilute (0.1 %–1 %) Fe:ZnO, alongside quenching of defect-related photoluminescence, both consistent with Fe incorporation into the lattice rather than into a secondary phase. The Kumar et al. (2011) sol-gel study traces the same trajectory more explicitly: the optical gap is "fast blue shifted in lower Fe-concentrations and after that slowly red shifted in higher Fe-concentrations", attributed by the authors to the Burstein–Moss effect throughout the doping range and to sp–d exchange at higher x. Maibam et al. (2020) likewise observe a large blue shift in band gap as dopant concentration increases, on the Burstein–Moss argument: the n-type nature of ZnO shifts the Fermi level into the conduction band as doping proceeds, and the optically measured gap then corresponds to transitions from the valence band into the unfilled conduction states above the Fermi level.

The physical picture is two-regime. At dilute Fe, the conduction band fills with carriers supplied by the donor-like Fe and by associated oxygen vacancies (Ali et al., 2023),(Esbergenova et al., 2024); the apparent optical gap widens because the lowest unoccupied states are now above the Fermi level (Burstein–Moss) (Nguyen et al., 2021). At higher Fe, the sp–d exchange interaction between localised Fe 3d electrons and the ZnO band electrons introduces a negative correction to the conduction-band edge and a positive correction to the valence-band edge, pulling the edges closer together and reverting to the band gap-narrowing regime widely used in photocatalysis (Singh et al., 2025). The regime crossover has been observed in the low doping concentration range depending on synthesis (Kumar et al., 2011)

In the benchmark that the Alharshan et al. (2023) study ran on wurtzite ZnO, the qualitative trend at higher Fe content in this study shows a blue-shift of the absorption edge from 380 nm to about 370 nm. Photocatalytic efficiency on methylene blue rises from 45% for pristine ZnO to approximately 72% for $Zn_{0.95}Fe_{0.05}O$ (Alharshan et al., 2023). These results, taken from the high-Fe side of the crossover, cannot be uncritically extrapolated to the dilute regime where blue shifts dominate.

The Ferromagnetism Controversy and the Bound Magnetic Polaron Framework

The prediction of hole-mediated ferromagnetism in transition-metal (TM)-doped ZnO (Bhardwaj et al., 2024) was carried over to Fe:ZnO, and a generation of experiments sought to confirm it. Subsequent experiments failed to confirm it over wide temperature ranges (Alshammari et al., 2023). More than two decades of research now show why: unambiguous evidence for long-range, carrier-mediated ferromagnetism remains elusive, and magnetic signals reported in many TM-doped oxide systems have instead been attributed to structural imperfections, dopant clustering, oxygen-vacancy complexes, or nanoscopic secondary magnetic phases (Kuryliszyn-Kudelska & Dobrowolski, 2026). Later experimental reports of room-temperature ferromagnetism in nominally undoped ZnO thin films attributed the signal to Zn vacancies, with sputtered films remaining ferromagnetic up to a very high Curie temperature of about 800 K (Hong et al., 2025). Within the surveyed literature, the most coherent framework for the surviving positive observations is the Bound Magnetic Polaron model (Venkatesan et al., 2004).

The model proceeds from defects rather than from bulk carrier statistics, in four linked steps. First, donor-type defects bind carriers locally: in ZnO, oxygen vacancies (V_O) and zinc interstitials (Zn_i) trap electrons in hydrogenic, 1s-like orbitals whose spatial extent is set by the defect's effective Bohr radius (Bhardwaj et al., 2024),(Alshammari et al., 2023); because the BMP model is particularly relevant to low-carrier-density systems (Bhardwaj et al., 2024). Second, through s–d exchange, the trapped electron exerts an effective exchange field on the surrounding Fe 3d spins, aligning them within its orbital radius; the total energy is minimised when the impurity spins lie parallel to this local field, producing the spin-polarised cloud that constitutes the bound magnetic polaron (Dietl, 2023),(Bhardwaj et al., 2024). Notably, the polaron mechanism accounts for both the formation and the ferromagnetic character of the interaction (Bukhtiar & Zou, 2024). Third, neighbouring polarons couple: two overlapping polarons lower their combined energy when their impurity clouds are aligned, which is to say when the two localised carriers are spin-parallel, so the polaron–polaron coupling is ferromagnetic (Bukhtiar & Zou, 2024). Fourth, long-range ferromagnetic order emerges only at percolation, when overlapping polarons form a continuous chain spanning the lattice (Chen et al., 2021). This is precisely why the model can accommodate room-temperature ferromagnetism at TM concentrations lying far below the percolation threshold for direct cation–cation exchange (Venkatesan et al., 2004). Within the same picture, a greater density of oxygen vacancies enlarges the total volume occupied by polarons, increasing their probability of overlapping more TM ions into ferromagnetic domains and thereby enhancing the ferromagnetic response (Verma, 2020). A further refinement concerns the Curie temperature (T_C): achieving a high $T_C$is associated with the dopant level crossing the Fermi level (Bhardwaj et al., 2024).

The most distinctive experimental signatures of BMP-mediated ferromagnetism follow directly from this picture. Magnetism should track defect density rather than dopant concentration alone; in substituted ZnO films, the ferromagnetism varies with the oxygen pressure used during growth, directly linking the magnetic signal to the defect concentration (Venkatesan et al., 2004). Transport provides a second signature, since the ferromagnetism in the insulating regime reportedly accompanies hopping transport (Behan et al., 2008). Measurements on doped ZnO further distinguish two magnetic regimes, a dilute magnetic semiconductor regime and a dilute magnetic insulator regime, governed by distinct magnetic mechanisms depending on carrier density (Behan et al., 2008).

Two caveats temper the model's appeal. Where magnetic ions sit close enough for direct overlap, oxygen-mediated superexchange prefers antiferromagnetic alignment and competes with BMP-induced ferromagnetic coupling (Chen et al., 2021). The identity of the operative defect is itself disputed, with different reports favouring oxygen vacancies, zinc interstitials, or zinc vacancies as the active species (Lage et al., 2021). In this connection, Dietl (2010)'s ten-year assessment makes the alternative possibility explicit: in the d^0 limit, ferromagnetism arises from spins of electrons residing on point or extended defects, with TM doping serving only to position the Fermi level at the relevant defect states.

The strongest, most reproducible ferromagnetism in Fe:ZnO found in the surveyed DFT and experimental literature is therefore either defect-mediated (zinc vacancies (V_{Zn}), oxygen vacancies (V_O), hole-doping) or phase-segregation-mediated ($ZnFe_2O_4$) (Kuryliszyn-Kudelska & Dobrowolski, 2026),(Elsheikh et al., 2022). In Fe-doped ZnO single crystals, three different regimes have been identified: dispersed Fe^{2+} and Fe^{3+} at low concentration and low processing temperature; $ZnFe_2O_4$ at very high processing temperature; and an intermediate regime with coexistence of metallic Fe (Fe^0) and ionic Fe, with ferromagnetism appearing only in the latter two cases (Zhou et al., 2008). The case for intrinsic bulk-lattice room-temperature ferromagnetism without such helpers is, on the available evidence, unconvincing.

Mg-Doped ZnO

Structural Response to Substitutional Mg

Substitutional Mg^{2+} enters the ZnO wurtzite lattice as a near-isovalent, slightly smaller cation (Yadawa et al., 2023). Our DFT+U calculations document the structural consequences in a ZnO supercell at 2.77% Mg: the in-plane lattice parameter a-axis expands from 3.2375 Å to 3.2489 Å, the out-of-plane parameter c-axis contracts from 5.2220 Å to 5.2066 Å, and the c/a ratio drops from 1.6129 to 1.6026. Zn–O bond distances d_1(Zn–O) and d_2(Zn–O) lengthen from 1.951 Å and 1.979 Å to 1.995 Å and 2.000 Å, respectively. The qualitative picture is consistent with other DFT reports: Mg is structurally a small perturbation of the wurtzite lattice and largely preserves local tetrahedral coordination (Jia et al., 2024),(Huang et al., 2022). The directional sign of the strain (a-axis expansion, c-axis contraction) is insensitive to whether U is applied to Zn 3d, because the host d-band plays no significant role in the substitutional geometry.

Substitutional Widening of the Direct Band Gap

The best-supported computed result on substitutional $Zn_{1-x}Mg_xO$ is an increase in the direct Γ to Γ band gap, as determined from CP2K DFT+U calculations and experiment (Lyons, 2025),(Khuili et al., 2023).

Configuration	Mg content	DFT-PBE /(eV)	DFT+U /(eV)	Experiment /(eV)
(b)	2.77%	0.753	3.370	3.380
(c)	5.55%	0.871	3.480	3.430
(d)	5.55% (alt.)	0.881	3.501	3.430
(e)	8.33%	0.902	3.567	—

The quadratic bowing implied by the data is small, consistent with the 0.18 eV bowing coefficient obtained from first-principles calculations on the same alloy series (Yin et al., 2017). The linear scaling band gap, $E_g(x) = 3.35 + 2.33x$, yields a band gap of E_g=4.29eV at x = 0.40 (Yin et al., 2017); photoabsorption measurements on highly c-axis oriented $Zn_{1-x}Mg_xO$ thin films report a 25% band gap enhancement by 30% Mg doping, with the optical gap tuned from 3.25 eV to 4.06 eV ($Zn_{0.7}Mg_{0.3}O$), confirmed by Wien2k GGA+scissor simulations (Kumar et al., 2013).

Mechanistically, the band gap widening in $Zn_{1-x}Mg_xO$ is driven by the modulation of the conduction band minimum (Takahashi et al., 2022). Photoabsorption measurements on $Zn_{1-x}Mg_xO$ thin films confirm the blueshift of the optical absorption edge, attributed to stress and crystallite size variations (Kumar et al., 2013).

Wurtzite-to-Rocksalt Transition as the Structural Ceiling

Substitutional and interstitial occupation of the cation site in ZnO produces structurally different effects (Zhang et al., 2025). Still, the dominant structural ceiling on Mg solubility in wurtzite ZnO is the wurtzite-to-rocksalt phase transition, not interstitial occupation alone. High Mg concentrations trigger interstitial incorporation, introducing significant lattice distortion and elevating the Fermi level (Zhang et al., 2025); at still higher Mg concentrations, the system undergoes phase separation into wurtzite and rocksalt structures (Piskunov et al., 2022).

The DFT study of Zn_xMg1–_xO solid solutions confirms the structural ceiling (Chak et al., 2026). The wurtzite-$Zn_{1-x}Mg_xO$ films with x > 0.4 typically consist of a wurtzite/rocksalt mixture due to phase separation, which limits the band gap to about 4.3 eV (Piskunov et al., 2022). For a hypothetical ZnO–magnesium oxide (MgO) pseudo-binary with a pure wurtzite or rocksalt structure, the band gap would be tunable from 3.3 eV to 7.8 eV with an operating range of 4.0 eV–6.0 eV (Piskunov et al., 2022), but achieving pure-phase material requires substrate engineering. It was shown that low-lattice-mismatch substrates such as scandium aluminium magnesium oxide ($ScAlMgO_4$), MgO, and copper(I) oxide (Cu_2O) can stabilise both the high-MgO-content wurtzite-$Zn_{1-x}Mg_xO$ and high-ZnO-content rocksalt-$Zn_{1-x}Mg_xO$ phases, breaking the conventional mutual solubility limit (Piskunov et al., 2022). The optical and ultraviolet-sensing literature has subsequently expanded to exploit these stabilised high-Mg phases (Ščajev et al., 2022). Recent calculations also indicate that rocksalt zinc magnesium oxide alloys are more resistant to hole-trapping than the wurtzite form, and remain p-type dopable in the rocksalt crystal structure (Lyons, 2025). The structural-stability picture therefore has multiple consistent strands: the wurtzite-to-rocksalt transition caps substitutional Mg, breaks the direct optical gap, and shifts the electronic character away from a useful wide-band-gap semiconductor unless non-equilibrium growth conditions are deliberately engineered.

RESULTS AND DISCUSSION

Comparative Synthesis

Open-shell Fe vs. Closed-shell Mg

A side-by-side comparison makes the contrast sharper. Fe introduces d–d transitions in high-spin states that induce visible-light optical absorption bands (Chithira et al., 2021). The Fe 3d states form shallow donor levels below the conduction band (Esbergenova et al., 2024), leaving the band-

edge structure recognisable but perturbed. has no corresponding behaviour in Mg-doped ZnO. Mg contributes minimal states near the band edges, so the band-edge structure remains dominated by the ZnO host (Huang et al., 2022).

Charge Transfer and Impurity States

The DFT perspective tightens the contrast still further. In Fe:ZnO, the O 2p–Fe 3d hybridisation facilitates visible-light absorption (Esbergenova et al., 2024), and Fe doping induces both Burstein–Moss widening and sp–d-exchange narrowing of the apparent band gap (Maibam et al., 2020),(Singh et al., 2025). In Mg:ZnO, the dominant charge rearrangement is local ion-by-ion: Mg^{2+} replaces Zn^{2+} on account of a smaller ionic radius, leading to lattice strain and a solid solution (Nur-E-Alam et al., 2025). No carrier injection occurs in the Mg case in the way Fe^{3+} injection (Singh et al., 2025) or oxygen-vacancy (V_O) formation does (Ali et al., 2023). This explains why Mg is not a candidate donor and does not interfere with optical transitions near the band edge, while Fe is both.

Technological Mapping

The bifurcation is genuine. Fe-doped ZnO has been proposed as a spintronic material and dilute magnetic semiconductor, within the bound magnetic polaron (BMP) framework, which requires explicit defect assistance (Verma, 2020) and as a photocatalytic host with absorption edges pushed into the visible (Esbergenova et al., 2024). At low Fe content, the same dopant acts as a band gap widener through the Burstein–Moss mechanism (Kumar et al., 2011), so the technological case is fundamentally composition-dependent. Mg-doped ZnO sits squarely in the UV-optoelectronics and solar-blind UV detector space (Du et al., 2009), with the important caveat that pushing Mg beyond the wurtzite-to-rocksalt solubility wall destabilises the structure (Ivanova et al., 2022). Systematic DFT exploration of co-doped ZnO (Fe + Mg) remains an underexplored corner of the literature and a natural route in principle to combine band gap engineering with controlled magnetism.

Controversies, Gaps and Open Questions

Reproducibility of Fe-induced ferromagnetism

We have described the disagreement in Section 4.4. Evidence indicates that ferromagnetism in Fe:ZnO often arises from secondary phases such as $ZnFe_2O_4$ or from defect-mediated mechanisms (Kuryliszyn-Kudelska & Dobrowolski, 2026). The BMP framework provides a coherent theoretical bridge between defect chemistry and experimental defect-mediated magnetism (Verma, 2020). Reproducible ferromagnetism in Fe:ZnO therefore seems, on the surveyed DFT evidence, to require either a defect-rich nanoparticle regime, a secondary magnetic phase, or co-doping.

Calculated Band Gaps: Method Dependence

The GGA-PBE band gap of pristine ZnO is significantly underestimated compared to experimental values (Achehboune et al., 2021); methods like GGA+U provide band gap estimates much closer to experimental measurements (Achehboune et al., 2021). Across the ZnO polymorphs, the band gap depends strongly on phase as well as functional: for wurtzite, zinc blende, and rocksalt ZnO, GGA gives 0.749, 0.637, and 0.817 eV, while GGA+U gives 1.12, 1.00, and 1.11 eV (Darma et al., 2015). The mBJ potential improves the wurtzite and zinc blende band gaps relative to GGA but overestimates the rocksalt band gap (Haq et al., 2013). Any cross-paper claim about an "Fe-induced band gap reduction from X /eV to Y /eV" must therefore be accompanied by its XC and polymorph specification. Two GGA-PBE papers comparing "X = 2.2 eV" to "Y = 1.6 eV" cannot be unambiguously compared to an HSE pair giving "X = 3.4 eV" vs. "Y = 2.9 eV" without explicit XC normalisation, and the Fe doping itself introduces a non-monotonic dependence on concentration that further complicates any one-shot comparison (Ali et al., 2023).

Choice of U: Empirical Fitting Versus Self-consistent Linear Response

A common protocol in the doped-ZnO literature is empirical U-tuning: pick a U that reproduces the experimental ZnO band gap, then apply it to the doped system (Yu et al., 2020). The Cococcioni & Gironcoli (2005) linear-response (LR) approach provides an internally consistent alternative in which U is derived from the system's own response to a localised perturbation; the Timrov et al. (2021) extension casts this into DFPT for production efficiency, and the Quantum ESPRESSO implementation provides a method for calculating U based on linear-response theory (Giannozzi et al., 2017). The implication for the surveyed Mg:ZnO work is that any quantitative claim about, say, the 3.56 eV band gap in the 8.33% Mg configuration should be re-examined under a LR-derived U before publication; the values reported remain credible but are not first-principles in the strict sense.

Supercell Finite-size Effects

Charged defects in particular require Madelung corrections and supercell sizes larger than 72 atoms for high accuracy (Jiang et al., 2024; Kumagai, 2023). Accordingly, conclusions regarding the relative energetic preference of surface sites for Fe^{2+} and Fe^{3+} should be interpreted cautiously and with explicit consideration of the associated uncertainties.

Wurtzite-rocksalt Transition vs. Interstitial Occupation

Recent studies of alkali-doped ZnO indicate that the rocksalt phase of ZnO and ZnxMg1−xO alloys can support p-type doping (Lyons, 2025), which would otherwise be considered irrelevant if interstitial wurtzite absorption continued to dominate. The interstitial-occupation analysis of Mg:ZnO remains relevant. Still, its importance is more limited than originally framed: it is a low-concentration perturbation pathway rather than the principal route by which the wide-band-gap character is destroyed.

Treatment of Disorder

All the substitutional Mg studies surveyed treat Mg as occupying a single ordered site, and the dopant–dopant interaction is inferred from a finite supercell. The interstitial-configuration analysis extrapolates from ordered supercells to a continuous composition but does not include the configurational entropy that a real Mg:ZnO nanocrystal would carry. Temperature-averaged occupancies of dopants across substitutional and interstitial sites remain an open computational frontier, and the failure to address disorder is in part responsible for the gap between DFT predictions and experimental observations in highly doped nanocrystals.

Absence of Vibrational and Finite-temperature Effects

Zero-Kelvin DFT predicts ground-state configurations only (Kiely et al., 2021). Standard *ab initio* methods describe only zero-temperature properties, omitting effects like thermal expansion. The temperature dependence of the band gap itself, $E_g(T) = 3.37 - 4.35 \times 10^{-4}\ T^2/(T + 310)$, is empirically known for ZnO (Liu, 2023) and should be carried into any comparison of DFT-predicted band gaps with experiment.

Reconciling Diffusion Monte Carlo (DMC) and Hybrid Functionals

The reported TDL+ΔCAS result (~4.94 eV) for wurtzite ZnO shows a discrepancy with the experimental value (~3.6 eV) (Laughon et al., 2022). The Leon et al. (2024) PBE0 (α = 0.22) and PBE+U (U_O = 7.5 eV, U_{Zn} = 9.5 eV) benchmark reproduces the room-temperature band gap and ARPES/XPS d-state binding energies simultaneously. These provide a direct cross-check on the same system. For the Fe:ZnO and Mg:ZnO configurations covered here, no comparable DMC benchmark exists. The published DFT-derived formation energies should be treated as semiquantitative where disordered or charged defects are involved.

CONCLUSION

Two narrative threads run through this review. The first is methodological: GGA-PBE on ZnO is qualitatively misleading on band gaps across all three well-known polymorphs, with reported values of 0.749, 0.637, and 0.817 eV for wurtzite, zinc-blende, and rocksalt ZnO (Darma et al., 2015). GGA+U with a tuned U on Zn 3d reduces the band gap error at moderate cost (1.12 eV, 1.00 eV, and 1.11 eV respectively) (Darma et al., 2015), and self-consistent linear-response U determination (Timrov et al., 2021) removes the need for empirical anchoring. Hybrid HSE and sX reproduce the band gap closely (Makkar & Ghosh, 2021); mBJ improves the band gap substantially for the wurtzite and zinc-blende phases but overcorrects the rocksalt phase (Haq et al., 2013). The choice of method is therefore not aesthetic: it determines which conclusions survive. Comparisons to structurally unrelated benchmark materials, such as the perovskite-structured $MgZnO_3$ (Lawati et al., 2023) with its six-coordinated Zn sites, should be avoided when assessing how well a functional describes wurtzite ZnO.

The second thread is the Fe-vs-Mg contrast itself. Fe brings spin, in-gap states (Singh et al., 2025), and a non-monotonic effect on the optical gap (Burstein–Moss widening at low Fe giving way to sp–d-exchange narrowing at higher Fe) (Kumar et al., 2011). The ferromagnetism mechanism is most coherently interpreted through the BMP framework (Verma, 2020): defect donors, not bulk Fe–Fe exchange, mediate spin alignment, and intrinsic bulk-lattice ferromagnetism without defect or secondary-phase assistance is, on the surveyed evidence, unconvincing (Zhou et al., 2008). Mg brings a controllable band-gap widening (Moriwake et al., 2025). Pushing the two dopants into the same supercell, a co-doping route, deserves attention at the DFT+U and hybrid-functional level.

Future progress will not come from cross-paper league tables of "best band gap" or "most accurate magnetic moment". It will come from treatments that explicitly handle finite-temperature disorder, dopant-defect complexes, polycrystalline nanoparticles, and kinetic effects. Phonon renormalisation of the band gap, free-energy methods for finite-T substitutional sites, machine-learning force fields parameterised against full-DFT references, and self-consistent linear-response U on dopant configurations are all on the near horizon. The reviewed literature provides the static, stoichiometric baseline; the field now needs to populate it with finite-T, multi-defect, actively-configurational data. Until then, and despite the respectable maturity of DFT on doped ZnO, the most consequential statement remains: the doping physics is settled in form, but not in detail.

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