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The YNiO₃ nickelate is a paradigm -electron oxide that manifests the intriguing temperature-mediated sequence of three phases transitions from (i) magnetically ordered insulator to (ii) paramagnetic (PM) insulator and then to (iii) PM metal. Such phenomena raised the question of the nature of the association of magnetism and structural symmetry breaking with the appearance in (i) and (ii) and disappearance in (iii) of insulating band gaps. It is demonstrated here that first-principles mean-field-like density-functional theory (DFT), driven by molecular dynamics temperature evolution, can describe not only the origin of the magnetically long-range ordered insulating phase (i), but also the creation of an (ii) that lacks spin- long-range order, and of a metallic paramagnet (iii) as temperature rises. This approach provides the patterns of structural and magnetic symmetry breaking at different temperatures, in parallel with band gaps obtained when the evolving geometries are used as input to DFT electronic band-structure calculations. This disentangles the complex interplay among spin, charge, and orbital degrees of freedom. Analysis shows that the success in describing the rise and fall of the insulating band gaps along the phase transition sequence is enabled by allowing sufficient flexibility in describing diverse local structural and magnetic motifs as input to DFT. This entails the use of sufficiently large supercells that allow expressing structural disproportionation of octahedra, as well as a description of PM phases as a distribution of local magnetic moments (rather than using a single averaged moment). It appears that the historic dismissal of mean-field-like DFT as being unable to describe such Mott-like transitions was premature, as it was based on consideration of averaged crystallographic unit cells, a description that washes out local symmetry-breaking motifs. The magnetically ordered insulating YNiO₃ phase (i) and the PM insulating phase (ii) result in DFT from allowing symmetry breaking, evident already by considering the athermal internal energy. In contrast, the PM metallic phase (iii) is formed thermally by smearing out thus weakening symmetry breaking. Analysis of snapshots of the different forms of structural vs magnetic symmetry breaking shows that only the loss of the polymorphous distribution of magnetic moments existing in (ii) causes the fall of the band gap, resulting in the metallic state in (iii). The interesting conclusion is that such a description of the rise [in phases (i) and (ii)] and fall [in phase (iii)] of the insulating gap does not rely on the traditional Mott-like strong correlation understanding, but on breaking and remaking of magnetic and structural symmetries reflected in energy lowering.

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I. INTRODUCTION

The insulating states both below and above the Néel temperature and the temperature-induced insulator-to-metal transition [1] are characteristic features of many 3 Mott oxide systems [2] that have been considered for neuromorphic computing [3] and transparent conductors [4–7]. From a fundamental perspective, the persistent pertinent questions continue to be (a) understanding the nature of the initial insulating phase that emerges from zero-gap band degeneracy associated with open-shell configuration [8,9]; (b) understanding the nature of the final metallic phase, which depends

Phase	Crystal space group	Magnetic order	Electronic properties	Temperature (K)	Structural motif	Magnetic motif
α	2_1 / (Monoclinic)	AFM	Insulator	< 145 [18,32,33]	B-DLE	M-DLE
β	2_1 (Monoclinic)	PM	Insulator	145 < < 582 [18,32,33]	B-DLE	M-DLE
γ	(Orthorhombic)	PM	Metal	>582 K [18]	B-SLE	M-SLE

TABLE I. Summary of the structural, magnetic, and basic electronic properties observed in different $YNiO_3$ phases. DLE denotes double local environment; SLE denotes single local environment, whereas "B" and "M" refer to bond and magnetic motifs.

[8,21–23] are mostly regarded as unresponsive background that is not the cause of the formation of (i)–(iii) but effects that can be considered later. This viewpoint caused an understandable migration of computational efforts that aim to describe phases (i)–(iii) of open-shell -electron oxides (e.g., YNiO₃ [24–28] and LaTiO₃ [10,13]) towards strongly correlated methods, leapfrogging mean-field–like methods such as DFT. However, it remains unclear if DFT was thought to fail in this problem because of its inability to describe strong correlation gap formation in the insulating phases (i) and (ii), or because of the lack of proper description of the local motifs in PM phases (ii) and (iii). For instance, it has been recently demonstrated that accounting for energy-lowering formation of distribution of local spin



FIG. 1. Octahedral volume (first row), local magnetic moments on Ni sublattice (second row), and electronic density of states (third row) from the first-principles calculations of $YNiO_3$. The four columns describe these results as obtained by a sequence of approximations: Column (a) uses a hypothetical monomorphous structure without symmetry breaking (SB), indicating a single characteristic volume and a simple distribution of local moments leading to a metallic zero band gap. Column (b) uses a spin polymorphous structure obtained by replacing an average monomorphous unit cell with a polymorphous supercell structure. This creates a distribution of different octahedral volumes and a



FIG. 2. Schematic illustration of (i-v) different moment (M) and bond (B) environments in YNiO₃ and transitions between them used to identify the band-gap opening and metallization. Bold frames denote physical phases from Table I.

SLE" can thus be represented by repeating as a single repeated motif ("monomorphous"). The next step [Fig. 2(ii)] illustrates a unit cell made of a mixed B-SLE with M-DLE, whereas Fig. 2(iii) illustrates the case of a bond-DLE (characterized by two different octahedra, small and large), and moment-DLE (characterized by two different magnetic motifs-zero or finite moment). Different periodic assemblies of bond- and moment-SLE and -DLE motifs make up phases of the crystal realized in crystallographic (monoclinic or orthorhombic) and spin (antiferromagnetic and paramagnetic). For example, the fully disproportionated unit cell of B-DLE/M-DLE can exist in an AFM monoclinic phase [Fig. 2(iii)], or as a PM monoclinic phase [Fig. 2(iv)], or a PM orthorhombic phase [Fig. 2(v), etc.].

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FIG. 5. Néel AFM α to PM

which splits degenerate bands into occupied and empty. We point out that the existence of a gapped PM phase can be naturally described by mean-field DFT without recourse to a strong correlation. This generally requires that one allows for a larger than a minimal unit cell, enabling structural and/or magnetic symmetry breaking. This leads to a polymorphous structure rather than a virtual averaged structure. Interestingly, YNiO₃ has two paramagnetic phases: one at low temperatures being a gapped insulator (β) and one at the higher temperature being ungapped metal (γ) . This poses an interesting conundrum as to how those behaviors existing in the same system can be understood. The interesting answer pointed out here is that a gapped insulating phase is evident in first-principles mean-field band theory already via minimizing the internal energy alone in an extended supercell. This leads to a polymorphous network having a distribution of both structural and magnetic motifs (whose average is the irrelevant monomorphous approximant). The motif distribution of this athermal polymorphous structure is inherited by the β phase observed in finite-temperature AIMD. As the temperature increases, AIMD shows that the distinct local structural and magnetic motifs lose their polymorphous distribution; when such geometries are used in band theory, a gapless metallic PM γ phase emerges. Thus, the metallic PM phase emerges from the insulating PM phase not necessarily because of loss of electron correlation but because of thermal motion-induced displacements that alter the electronic band structure.

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APPENDIX: DFT DETAILS

The first-principles calculations are carried out using plane-wave DFT + as implemented in the Vienna Simulation Package (VASP) [38-40] with PBEsol (Perdew-Burke-Ernzerhof (PBE) functional revised for solids) [41]. For all calculations, a rotationally invariant approach introduced by Dudarev [42] with - values of = 2 eVand = 0 applied on Ni- states is utilized. We recall that in DFT + acts primarily to reduce the mean-field selfinteraction in DFT, and thus does not have the same role as in Hubbard model (i.e., strong correlation). The cutoff energies for the plane-wave basis are set to 500 eV for final calculations and 550 eV for volume relaxation. Atomic relaxations are performed until the internal forces are smaller than 0.01 eV/Å unless specified. Analysis of structural properties and visualization of computed results are performed using VESTA [43] and PYMATGEN library [44]. The paramagnetic phase of YNiO₃ is simulated by using the special quasirandom structure [45] by decorating a 160-atom supercell with spin up and spin down to create a global zero-moment configuration closest to the high-temperature limit of a random spin paramagnet [31]. AIMD simulations are done using the

ensemble with an thermostat for 30 ps with the time step of 1 fs. For AIMD simulations, the averaged density of states for snapshots has been calculated from molecular dynamics snapshots as $DOS = \frac{\sum DOS}{2}$, where DOS of different snapshots are aligned using O-1 core states. The volume of each octahedron was calculated as the convex hull volume for each octahedron. For each AIMD simulation, 200 snapshots are extracted from molecular dynamics simulations after an equilibration period of 10 ps. The distribution of magnetic moments and density of states are computed by averaging of corresponding quantities for 40 snapshots of

molecular dynamics simulations after equilibration for 10 ps. The DOS for different snapshots is aligned using O-1 core states.