A-site hybridization wave induced Mott transition in ABO₃ perovskites

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Correlated insulators in quantum materials including ABO₃ perovskites are traditionally classified as Mott-Hubbard or charge-transfer insulators, focusing exclusively on the B-site cation and the ligand (oxygen). In this work, we propose a unique kind of hybridization wave induced Mott insulator, where a spatial modulation in the hybridization between the ligand and the A-site cation triggers a Mott transition on the correlated B-site transition metal cation. Our work is relevant to a variety of ABO₃ perovskites such as BiNiO₃ and PbCrO₃ with A-site cations having extended 6s orbitals. Using ab initio electronic structure and slave rotor theory, we show that pressure tunes the ligand energy, driving a colossal volume-changing Mott transition, as observed in these compounds, from a Mott insulator induced by an A-O hybridization wave into a uniform metal at high pressure.

The seminal work of Zaanen, Sawatzky and Allen (ZSA) [1] highlighted the key role of the ligand ion in understanding the correlated insulating phases of transition metal (TM) oxides and halides, and their associated metal insulator transitions (MITs). This allows us to distinguish Mott-Hubbard insulators, such as V₂O₃ or Ti₂O₃ [2], from charge-transfer insulators, such as CuO or NiCl₂ [3]. In recent years, interest in MITs has been rejuvenated by extensive experimental [4–20] and theoretical [21–30] work on ABO₃ perovskite based rare-earth nickelates and their heterostructures. In these RNiO₃ compounds, varying the size of R ion tunes the Ni-O-Ni bond angle, and the MIT (in all cases except LaNiO₃ which remains metallic [3]) is driven by a combination of the resulting reduction in band-width and a spontaneous charge disproportionation MIT occurring in materials like BiNiO₃, as observed in these compounds, from a Mott insulator induced by an A-O hybridization wave into a uniform metal at high pressure.
specific example, we find that when the oxygen level energy is closer to that of Bi, the large overlap between the Bi 6s and oxygen orbitals permits a Bi-O hybridization wave instability, which leads to a three-dimensional (3D) checkerboard pattern of alternately compressed and expanded BiO$_{12}$ polyhedra. This results in suppression of the effective Ni-O hybridization, and triggers a Mott transition due to strong correlations on the B-site Ni ions. We show that increasing pressure effectively shifts the ligand energy level position, favoring Ni-O hybridization over Bi-O hybridization, and eventually killing the Bi-O hybridization wave. This leads to a metallic phase, dominated by Ni-O states at the Fermi level, which, unlike the rare-earth nickelates [24, 25], is stable against a ‘charge disproportionation’ MIT on Ni due to the much stiffer Ni-O bonds in the volume-collapsed metal. We suggest that materials like BiNiO$_3$ and PbCrO$_3$ may provide remarkable examples of an A-site hybridization wave stabilized Mott insulator, which can undergo a transition into a uniform metal under pressure, temperature, or isovalent A-site substitution [33, 34]. Our findings inspire us to predict further material candidates for such colossal volume-changing MITs induced by pressure.

Pressure-induced structural transition. - At ambient pressure (AP), the crystal structure structure of BiNiO$_3$ is triclinic with two inequivalent Bi sites, Bi1 and Bi2, and four inequivalent Ni sites, Ni1–Ni4, which undergoes a structural transition into a high pressure (HP) orthorhombic phase with equivalent Bi and Ni sites, above 3.5GPa [41]. This produces a staggered pattern of alternately compressed and an expanded BiO$_{12}$ polyhedra in the AP phase, while the HP phase features BiO$_{12}$ polyhedra of uniform volume. We begin by describing this pressure-induced structural transition within DFT.

The DFT total energy and electronic structure calculations have been carried out in pseudo-potential plane-wave basis with generalized gradient approximation (GGA) [42] supplemented with Hubbard $U$ (GGA+U) [43] ($U = 4$ eV, $J_H = 0.9$ eV), as implemented within Vienna-Abinitio-Simulation-Package (VASP) [44]. See Supplementary Material (SM) for details.

We have studied both triclinic and orthorhombic crystal structures at different unit cell volumes, between the AP volume and that reduced by 7% with respect to AP at 6GPa, and replacing Ni ions by a uniform positive background, we calculated the energy change $\delta E$ upon making a small displacement of oxygen atoms ($\delta O$) from their equilibrium positions; see Fig. 1(b) inset. Fitting $\delta E = \frac{1}{2} k(\delta O)^2$ yields the Bi-O bond stiffness constants $k_{\text{BiO}} = 2.06\text{eV/Å}^2$ and $2.32\text{eV/Å}^2$ for AP and 6 GPa HP volumes, respectively. For the Ni-O sublattice, as shown in Fig. 1(b), a similar calculation yields corresponding values $k_{\text{NiO}} = 7.96\text{eV/Å}^2$ and $10.84\text{eV/Å}^2$. Thus, the Ni-O bond is about four times as stiff as the Bi-O bond at AP, and becomes substantially stiffer at HP. We propose this as an explanation for the observed absence of a breathing mode distortion of NiO$_6$ octahedra in the HP phase, and the resulting stability of the volume-collapsed metal against a Ni ‘charge-disproportionation’ MIT.

DFT electronic structure.- Fig. 2(a) shows the spin-polarized GGA+U density of states (DOS) of AP and HP (7GPa) BiNiO$_3$, respectively, projected onto Bi-s, Ni-d and O-p states. The Ni-d and O-p plots are the DOS averaged over four inequivalent Ni sites in AP, and six and two O sites in AP and HP, respectively.

At AP, our DFT calculation gives rise to an antiferromagnetic (AFM) Slater insulator. We further find that both Bi1 and Bi2 sites have filled 6s states deep in energy $\approx 10.5$eV below Fermi level ($E_F$). The split-off, unoccupied part of Bi2-s states, which are at $\approx 1$eV above $E_F$, and well-separated from the filled Bi2-s states by a large energy separation of $\approx 9-10$eV, is entirely derived from strong admixture with O-p states (see encircled regions in the figure). The contribution of Ni-d to this split-off state is nonzero but small. We find the Ni-d states to be filled in the majority spin channel, while the octahedral crystal-field split Ni-t$_{2g}$ and Ni-e$_{g}$ states are filled and empty (positioned beyond the energy shown in the figure), respectively in minority spin channel. This suggests the stabilization of [Bi$_{1.5}$(Bi$^{3+}$/L$^{2-}$)$_{0.5}$][Ni$^{2+}$/L$^{6-}$] configuration in AP, instead of the proposed [Bi$_{1.5}$(Bi$^{2+}$/L)$^{2-}$][Ni$^{2+}$] configuration in AP, instead of the proposed [Bi$_{1.5}$(Bi$^{2+}$/L)$^{2-}$][Ni$^{2+}$] configuration in AP.
this picture in BiNiO$_3$ hole changes character from Bi-s, like Ni-d, and O-p. The zero of the energy is set at GGA+$U$ Fermi energy. In the AP, the DOS projected to Bi1 (solid, black) and Bi2 (shaded) are shown separately.

(b) Calculated energy level positions of Bi-s, O-p and Ni-$e_g$ in AP and HP phase of BiNiO$_3$. The zero of the energy is set at the average on-site energy of Ni-$e_g$ in both phases.

Fig. 2. (Color online) (a) Spin-polarized GGA+$U$ projected density of states of BiNiO$_3$ in AP (top panels) and HP (bottom panels) phase. Left, middle and right panels show DOS projected to Bi-s, Ni-d, and O-p. The zero of the energy is set at GGA+$U$ Fermi energy. In the AP, the DOS projected to Bi1 (solid, black) and Bi2 (shaded) are shown separately.

(b) Calculated energy level positions of Bi-s, O-p and Ni-$e_g$ in AP and HP phase of BiNiO$_3$. The zero of the energy is set at the average on-site energy of Ni-$e_g$ in both phases.

figuration. This is supported by the calculated average magnetic moment of $\approx 0.1\mu_B$ at oxygen site, an unexpectedly large moment contrary to the expectation of $\approx \mu_B$.

For strong correlations, $U/\mu_B = 6.5$, decreasing $\epsilon_D - \epsilon_O$ leads to a transition from an distorted insulator (DI) to an undistorted metal (UM). (b) At small $U/\mu_B = 2.5$, the DI phase gets replaced by a distorted insulator (DI) to an distorted metal (DM). (c) DOS $N_{\text{tot}}(\omega)$ for typical points in the AP and HP phases, marked by stars in (a), showing a Mott gap in the DI phase and metallic DOS in the HP metal. Also shown is the metallic DOS for a metastable phase at point marked AP, with imposed zero distortion $\varphi = 0$.

At HP, the DFT calculation gives rise to a metallic solution, with dispersive bands crossing the Fermi level. This reproduces the observed MIT between the HP metal and magnetic AP phase. Our DFT total energy calculations shows stabilization of FM Ni-Ni interactions; we therefore predict the HP phase should be a FM metal or exhibit strong FM correlations. Analyzing the projected O-p DOS, we again find significant weight at the unoccupied part, reflecting the presence of a ligand hole. However, the unoccupied part of O-p states have lot more Ni-d character, and much less Bi-s character, compared to the AP phase. Interestingly, the magnetic moment on Ni site in the HP phase ($1.48\mu_B$) is only slightly smaller than in the AP phase ($1.73\mu_B$), in marked contrast to proposal of Ni$^{3+}$ to Ni$^{3+}$ valence transition between AP and HP. The DFT results thus suggests stabilization of [Bi$^{3+}L^{\pm}\frac{1}{2}$][Ni$^{2+}L^{1-\pm}$] configuration in HP. The validity of this picture in BiNiO$_3$ is supported by Ni K-edge X-ray absorption spectroscopic study [47]. Calculation of crystal orbital Hamiltonian population (COHP) [48], as presented in SM, corroborates our conclusion that the ligand hole changes character from Bi-s like to Ni-d like.

What causes this shift of oxygen covalency under pressure? To answer this, we show in Fig. 2(b), the computed Bi-s, Ni-$e_g$ and O-p energy level positions in AP and HP phases, obtained from the tight-binding representation of the low-energy Hamiltonian in Wannier function basis within the N-th order muffin-tin-orbital (NMTO) formulation of downfolding technique [19, 50]; for details see SM. For AP phase, the s-level energy positions of two Bi ions, differ by about 1.5eV, Bi2-s being closer to O-p compared to Bi1-s, justifying a stronger covalency between Bi2-s and O-p, and ligand holes being associated with Bi2 rather than with Bi1. In the HP phase, the energy difference between Bi-s and O-p is similar to that between Bi1-s and O-p in AP phase, while the energy difference between Ni-d and O-p gets markedly reduced.

Slave rotor theory. — To clarify the role of strong correlations in the material, we next investigate the general A and B site-active perovskite problem in a DFT-inspired $s$-$p$-$d$ type model rather than a conventional $p$-$d$ model, retaining the A-site ion, and treating the ligand level as a pressure-tunable parameter. While our DFT study is crucial in identifying the main ingredients of this model, we focus here on Mott transition of the B-site TM ion using slave rotor theory [51, 52] for a simplified model Hamiltonian. This allows one to: (i) focus on a few key degrees of freedom, (ii) emphasize the strong correlation aspect, and (iii) easily explore a larger parameter space.
We denote the on-site energies on A, B, and oxygen to be $\epsilon_A$, $\epsilon_B$, and $\epsilon_O$, and fix $\epsilon_B = 0$. Denoting A-O and B-O hopping amplitudes in the symmetric phase as $t_A$, $t_B$ respectively, and a Hubbard repulsion by $U > 0$ on B, yields the Hamiltonian $H = H_1 + H_2 + H_3 + H_4$, with

$$H_1 = \epsilon_A \sum_{\mathbf{r},\sigma} a_{\mathbf{r}+\Delta,\sigma}^\dagger a_{\mathbf{r}+\Delta,\sigma} + \epsilon_O \sum_{\mathbf{r},\sigma} c_{\mathbf{r},\sigma}^\dagger c_{\mathbf{r},\sigma}$$

$$H_2 = -t_B \sum_{\mathbf{r},\sigma,\delta} \sum_{\mathbf{r}',\sigma,\delta'} g_{\mathbf{d}_{\sigma,\delta}} \left[ b_{\mathbf{r}',\sigma}^\dagger \left( \ell_{\mathbf{r}',\Delta,\sigma} + \ell_{\mathbf{r}',-\Delta,\sigma} \right) + \text{h.c.} \right]$$

$$+ \sum_{\mathbf{r},\sigma} U \sum_{\mathbf{r},\sigma,\alpha} b_{\mathbf{r},\sigma}^\dagger b_{\mathbf{r},\sigma} b_{\mathbf{r},\alpha}^\dagger b_{\mathbf{r},\alpha} - 2)^2$$

$$H_3 = -t_A \sum_{\mathbf{r},\delta,\eta_a,\sigma} \left[ 1 + \varphi(-1)^r \right] \left( a_{\mathbf{r}+\Delta,\sigma}^\dagger c_{\mathbf{r}+\Delta+\eta_a,\sigma} + \text{h.c.} \right)$$

$$H_4 = 12 N \times \frac{1}{2} \kappa \varphi^2$$

where $a$, $b$, $\ell$, $\delta$ denote electron operators on A, B, and ligand site respectively, with $\alpha$ labelling the $b$-orbitals. Here $H_1$ describes the on-site energy, with a choice $\epsilon_A = 0$, while $H_2$ and $H_3$ respectively describe the A-O and B-O electronic Hamiltonians, and $H_4$ denotes the elastic energy cost of A-O bond deformations. Using DFT input, we assume the much stiffer B-O sublattice to be immune to breathing distortion. We allow for a staggered A-O hopping, $t_A(1 \pm \varphi)$ with $\varphi \neq 0$, in order to describe the A-O hybridization wave. In the symmetric phase $\varphi = 0$. In the distorted phase $\varphi = \varphi(\mathbf{d}_{\sigma,\delta})$, where $\beta \equiv \left( \partial \ln t_A / \partial \ln \kappa_{\mathbf{d}_{\sigma,\delta}} \right)$, and $\delta_{\mathbf{d}_{\sigma,\delta}}$ is the change in A-O bond length compared to its undistorted value $\kappa_{\mathbf{d}_{\sigma,\delta}}$. The elastic energy cost in $H_4$ is $\frac{1}{2} \kappa \varphi^2$ per bond, where $\kappa = k a_{\mathbf{d}_{\sigma,\delta}}^2 / \beta^2$, with spring stiffness constant $k$, and with 12N A-O bonds. For BiNiO$_3$, as described below, we have two $e_g$ orbitals (1 $d_{x^2-y^2}$ and 2 $d_{3z^2-r^2}$) at the B-site, with $g_{1,s}/g_{1/2} = \{1, -1, 0\}$ and $g_{2,s}/g_{1/2} = \{25, -1, -1\}$ to model orbital-dependent hopping from B-site to neighboring ligands. Our model can be trivially extended to the case of $t_{2g}$ orbitals relevant to Cr in PbCrO$_3$.

We have studied the zero temperature phase diagram of Hamiltonian $H$ using a single-site slave rotor approach on the B-site (see SM for details). We work in units with $t_B = 1$. Motivated by DFT, we choose $(\epsilon_A - \epsilon_B)/t_B = 8$, $t_A/t_B = 2.5$, and vary $k$ and $\epsilon_O$, with $\epsilon_A < \epsilon_O < \epsilon_B$. We have checked that some variation in these parameters does not qualitatively affect our main results below.

Fig. 3 shows the phase diagram as we vary the ligand energy and stiffness $k$, for a B-site ion with (a) strong correlations, $U/t_B = 6.5$, and (b) weak correlations, $U/t_B = 2.5$. For fixed $k$, when $\epsilon_O$ is close to $\epsilon_B$, the ground state is an undistorted metal (UM) with non-integer Ni $e_g$ occupancy $n_{Ni}$. Tuning $\epsilon_O$ away from $\epsilon_B$ (i.e., towards $\epsilon_A$) leads to a first-order transition into either a distorted Mott insulator (DI) with pinned $n_{Ni} = 2$, or a distorted metal (DM), depending on $U$. The strongly correlated case, with $U/t_B = 6.5$ on B-site, where tuning $\epsilon_O$ leads to a Mott localized DI, mimics the Ni site in BiNiO$_3$; for $t_B = 0.75eV$, we get $U \approx 5eV$. Thus, the spontaneous checkerboard modulation of the A-O bond hybridization $\pm \varphi$ cooperates with a large $U$ on the B-site to induce this hybridization-wave driven Mott insulator. The critical value $(\epsilon_B - \epsilon_O)_{crit}$ for the MIT increases with the A-O bond stiffness (which increases $k$). At the indicated point in the DI phase in Fig. 3(a), with $k \approx 0.25$, the optimal distortion $\varphi \approx 0.55$. Choosing $\beta \approx 5 \approx 55$ and $a_{\mathbf{d}_{\sigma,\delta}} = 2.3A$ yields $\delta_{\mathbf{d}_{\sigma,\delta}} \approx 0.25A$ as seen in BiNiO$_3$. Setting $t_B = 0.75eV$, we get $(\epsilon_B - \epsilon_O)_{crit} \approx 3.8eV$ for metallization, while the $k$ value translates into a stiffness $k \approx 1eV/A^2$, both in reasonable agreement with DFT, given that our model includes a single ligand orbital and simplified interactions. The DOS, as shown in Fig. 3 (c), displays a Mott gap in the DI phase while it is metallic in the UM phase. Forcing the distortion to zero ($\varphi = 0$) in the regime of the DI phase leads to a metallic DOS (see Fig. 3(c)); correlations alone are thus insufficient to induce an insulator. Fig. 3(c) inset shows how the Ni $e_g$ occupancy varies with $\varphi$ at point AP, getting pinned to 2 electrons in the optimally distorted Mott insulator.

**Bond dependent hybridization.** — Figs. 4 (a)-(d) shows the bond-dependent kinetic energy on the Bi-O and Ni-O bonds computed from the model Hamiltonian. In the DI phase, the Ni-O hybridization is weak, while alternate BiO$_{12}$ polyhedra have strong and weak hybridization with surrounding oxygens. In the UM phase, on the hand, the Ni-O hybridization strengthens significantly compared to that in insulating phase, while the Bi-O hybridization becomes uniform. This observation is corroborated by NMTO-downfolding-derived Wannier function plots of O-p only basis calculations shown in Fig. 4(e),

![FIG. 4. (Color online) Bond-dependent kinetic energy obtained from model Hamiltonian (magnitude indicated in color bar) on (a) Ni-O and (b) Bi-O sublattices in the AP phase, projected to $xy$ plane. Corresponding plots for HP phase are shown in (c) and (d). (e) Constant amplitude surface of O-p Wannier functions from DFT for BiNiO$_3$ in AP structure, superposed on a pair of NiO$_6$ octahedra with adjacent two Bi ions, showing strong Bi2-O overlap and weaker Ni-O and Bi1-O overlaps; cyan (light grey) and magenta (dark grey) colors indicate opposite signs. (f) Same as (e) but for HP; here overlap of Ni-O is enhanced and Bi2-O is suppressed.](image-url)
In the AP phase, the Wannier function is highly asymmetric, having a pronounced tail at Bi2 and nearly vanishing at Bi1. In the HP phase, on the other hand, it is symmetric between the Bi sites. Further, upon moving from AP to HP the tail at the Ni sites is strengthened significantly, as in the model calculations. This highlights the change in character of the ligand hole, from Ni d-like to Bi s-like, across the MIT with decreasing pressure.

**Conclusion.** Using DFT and slave rotor calculations, we have established that the unusual insulating phases in compounds like BiNiO3 or PbCrO3 are A-site hybridization wave driven Mott insulators, which undergo a pressure-induced volume-collapse MIT. We have identified the key ingredients for this phenomenon as the extended (6σ) orbital of the A site, and strong correlations and appropriate filling on the B site, with the ligand energy being tuned by pressure. Based on our study, we expect such phenomena to be realized in many other materials; we propose materials like TlMnO3-like, across the MIT with decreasing pressure.

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[45] The supplemental material contains detailed information regarding: (i) crystal structures, (ii) DFT computations,
O-Ni-O deviates from 90°.

Ni-O-Ni between... 152° from 90°.

The NiO bond length 2.06 Å in Ni₃O₆ octahedra, from 1.99 to 2.12 Å with average bond length 2.08 Å in Ni₂O₆ octahedra, from 2.05 to 2.07 Å with average bond length 2.06 Å in Ni₃O₆ octahedra, from 2.04 to 2.15 Å with average bond length 2.08 Å in Ni₄O₆ octahedra. The Ω-Ni-O deviates from 90° by 2 to 5°, 2 to 8°, 0 to 9° and 4 to 10° in Ni₁O₆, Ni₂O₆, Ni₃O₆ and Ni₄O₆, respectively. The NiO₆ octahedra are tilted, as well as rotated with Ω-Ni-O-Ni ranging from about 133° to about 145°. The volume of Bi₁O₁₂ is larger than Bi₂O₁₂ by 5.26 Å³. The Bi-O bond lengths in Bi₁O₁₂ and Bi₂O₁₂ vary from 2.16 to 3.60 Å and from 2.04 to 3.70 Å respectively.

In the HP, orthorhombic structure on the other hand, the Ni-O bond lengths are

... 153°.

The Bi-O bond length vary between 2.24 and 3.28 Å.

Appendix

I. Crystal Structure

Crystal structures of BiNiO₃ in AP phase with PT symmetry and in HP phase (6 GPa) with Pbnm symmetry, are shown in Fig. 5 (a) and (b) respectively. The unit cell of BiNiO₃, in both AP and HP phase, contains four formula units with 20 atoms in the cell. The triclinic AP phase has four inequivalent Ni atoms, Ni₁...Ni₄, and two inequivalent Bi atoms, Bi₁ and Bi₂, while the orthorhombic HP phase has only one inequivalent Ni and one inequivalent Bi atoms in the cell.

In the AP phase, the Ni-O bond lengths vary from 1.99 to 2.20 Å with average bond length of 2.09 Å in Ni₁O₆ octahedra, from 1.99 to 2.12 Å with average bond length 2.08 Å in Ni₂O₆ octahedra, from 2.05 to 2.07 Å with average bond length 2.06 Å in Ni₃O₆ octahedra, from 2.04 to 2.15 Å with average bond length 2.08 Å in Ni₄O₆ octahedra. The Ω-Ni-O deviates from 90° by 2 to 5°, 2 to 8°, 0 to 9° and 4 to 10° in Ni₁O₆, Ni₂O₆, Ni₃O₆ and Ni₄O₆, respectively. The NiO₆ octahedra are tilted, as well as rotated with Ω-Ni-O-Ni ranging from about 133° to about 145°. The volume of Bi₁O₁₂ is larger than Bi₂O₁₂ by 5.26 Å³. The Bi-O bond lengths in Bi₁O₁₂ and Bi₂O₁₂ vary from 2.16 to 3.60 Å and from 2.04 to 3.70 Å respectively.

In the HP, orthorhombic structure on the other hand, the Ni-O bond lengths are ≈ 1.95 Å and the Ω-Ni-O deviates from 90° by ≈ 2°. The NiO₆ octahedra are less tilted in comparison to triclinic structure with Ω-Ni-O-Ni between 152° and 153°. The Bi-O bond length vary between 2.24 and 3.28 Å.

II. DFT Computational Details

The DFT calculations have been carried out with the choice of two different basis sets: (a) the plane-wave based basis as implemented in the Vienna ab initio Simulation Package (VASP), (b) the muffin-tin orbital (MTO) based linear muffin-tin orbital (LMTO) and the Nth order MTO (NMTO) method, as implemented in the STUTTGART code. The consistency of the calculations in two different basis sets has been cross checked in terms of calculated density of states and band structure.
FIG. 5. (Color online) (a) The triclinic ($P\bar{1}$ symmetry) and (b) the orthorhombic ($Pbnm$ symmetry) crystal structures of BiNiO$_3$. The two inequivalent Bi and four inequivalent Ni sites in triclinic structure, are marked while single inequivalent Bi and Ni sites in orthorhombic structure are marked.

The structural optimization as well as total energy calculations have been carried out in the plane wave basis with projector-augmented wave (PAW) potentials. During the structural optimization the atomic positions have been relaxed maintaining the symmetry of the crystal and volume of the cell. The positions of the atoms were relaxed towards equilibrium until the Hellman-Feynman forces became less than 0.01 eV/Å. A plane-wave cutoff of 600 eV and Monkhorst-Pack k-point mesh of $10 \times 10 \times 10$ for $P\bar{1}$ and $Pbnm$ symmetry were found to provide a good convergence of the total energy.

The construction of low energy Hamiltonian in first principles derived Wannier function basis was achieved through NMTO-downfolding technique starting from a full DFT band structure. The NMTO calculations have been carried out with the potential obtained from self-consistent LMTO calculation. The exchange-correlation functional was chosen to be that of generalized gradient approximation (GGA) implemented following the Perdew-Burke-Ernzerhof (PBE) prescription. To account for the effect of strong electron-electron correlation at magnetic Ni ion, the missing correlation beyond GGA was taken into account through supplemented Hubbard $U$ (GGA+$U$) calculation. For the $U$ values we chose the typical values for 3$d$ transition metal oxides. The muffin tin radii for the LMTO calculations were chosen to be 1.52, 1.44, 1.33, 1.32, 1.38, 0.97, 1.04, 1.03, 1.07, 1.04 and 1.04 Å for Bi1, Bi2, Ni1, Ni2, Ni3, Ni4, O1, O2, O3, O4, O5 and O6 respectively in case of triclinic structure, and 1.59, 1.29, 1.04 and 1.04 Å for Bi, Ni, O1 and O2 respectively, for the orthorhombic structure.

The exchange-correlation functional was chosen to be that of generalized gradient approximation (GGA) implemented following the Perdew-Burke-Ernzerhof (PBE) prescription. To account for the effect of strong electron-electron correlation at magnetic Ni ion, the missing correlation beyond GGA was taken into account through supplemented Hubbard $U$ (GGA+$U$) calculation. For the $U$ values we chose the typical values for 3$d$ transition metal oxides. The results reported in the following have been obtained for $U$ (Ni) = 5 eV, with Hund's coupling, $J_H$ of 0.9 eV. We have checked the validity of our results by varying the $U$ value by ±1-2 eV at Ni site. The trend in the results was found to remain unchanged.

III. Crystal Orbital Hamiltonian Population (COHP)

In order to characterize the change in the nature of metal-ligand covalency, and consequent change in the character of the ligand hole in a rigorous manner, we calculated the crystal orbital Hamiltonian populations (COHPs). The crystal orbital Hamiltonian population, COHP, which is the density of states weighted by the corresponding Hamiltonian matrix element, is a tool that permits energy-resolved analysis of pairwise interactions between atoms. It is indicative of the strength and nature of a bonding (negative COHP) or antibonding (positive COHP) interaction. The Fig. 6(a)
FIG. 6. (Color online) (a) The Bi-O COHPs and (b) Ni-O COHPs, in the AP and HP BNO. The HP Bi-O and Ni-O are shown in red connected circles, while the AP Ni-O COHP is shown in solid, black with AP Bi1-O and AP Bi2-O COHPs shown as solid, black and shaded area, respectively.

and (b) shows the calculated Bi-O and Ni-O COHP respectively, in AP BiNiO$_3$ in comparison to that in HP phase. For the AP phase, the Bi1-O and Bi2-O COHP have been plotted separated, which show a marked difference between themselves. As is seen from the plots, just above the Fermi level, the Bi2-O COHP of AP BNO shows a large peak, which is suppressed in both Bi1-O COHP of AP BNO, and Bi-O COHP of HP BNO. Moving onto Ni-O COHP, we find that the HP Ni-O COHP in the unoccupied part extends far more in energy compared to AP average Ni-O COHP, the integrated weight of the HP Ni-O COHP above E$_F$ being substantially larger compared to that of AP Ni-O COHP. This corroborates the view that the ligand hole changes its character from more Bi-$s$-like to more Ni-$d$-like in moving from AP to HP.

IV. Slave rotor theory

A. The Model

The Hamiltonian discussed in the main paper has the form

$$H = H_1 + H_2 + H_3 + H_4$$

$$H_1 = \epsilon_B \sum_{r,\sigma,\alpha} b_{\alpha,r,\sigma}^\dagger b_{\alpha,r,\sigma} + \epsilon_A \sum_{r,\sigma,\alpha} a_{r+\Delta,\sigma}^\dagger a_{r+\Delta,\sigma} + \epsilon_{Ox} \sum_{r,\sigma,\delta} \ell_{\delta,r+\delta,\sigma}^\dagger \ell_{\delta,r+\delta,\sigma}$$

$$H_2 = -t_B \sum_{r,\sigma,\delta} g_{\alpha,\delta} (b_{\alpha,r,\sigma}^\dagger [\ell_{\delta,r+\delta,\sigma} + \ell_{\delta,r-\delta,\sigma}] + \text{h.c.}) + \frac{U}{2} \sum_{r} (\sum_{\alpha,\sigma} b_{\alpha,r,\sigma}^\dagger b_{\alpha,r,\sigma} - 2)^2$$

$$H_3 = -t_A \sum_{r,\delta,\eta_\delta,\sigma} [1 + \varphi(-1)^{x+y+z}] (a_{r+\Delta,\sigma}^\dagger \ell_{\delta,r+\Delta+\eta_\delta,\sigma} + \text{h.c.})$$

$$H_4 = 12N \times \frac{1}{2} \kappa \varphi^2$$

Here, the subscript $\alpha$ in $b_{\alpha,r,\sigma}^\dagger$ refers to the orbital index (which takes on two values $\alpha = 1, 2$ corresponding respectively to $d_{x^2-y^2}, d_{3z^2-r^2}$), $\Delta$ is the Bi position within the unit cell, and $\eta_\delta$ refers to the locations of the $p_\delta$-oxygen atoms relative to the Bi atom. For example, $\eta_\delta = \pm (0, \frac{1}{2}, \pm \frac{1}{2})$ refers to the four $\ell_\delta$ oxygen positions relative to the Bi atom at the cube center. Finally, the factor of 12 in the elastic energy refers to the 12 Bi-O bonds within each cube, and $N$ is the number of Ni atoms (viz. unit cells in the undeformed high pressure phase). The energies are measured relative to the atomic Bi energy or the A site energy, setting $\epsilon_A = 0$ to fix the zero of energy. Note that in scaled
units, $t_B = 0.75$, $t_A/t_B = 2.5$, $U/t_B = 6.5$, $\epsilon_B/t_B = 8$. Two orbitals were considered on Ni (the B site) that have different hopping amplitudes determined by $g_{a\delta}$, to mimic orbital dependent hopping. To resemble hopping from $e_g$ orbitals ($1 : d_{x^2−y^2}, 2 : d_{3z^2−r^2}$) to a s-like oxygen orbital, $g_1,2/\sqrt{2} = \{1,−1,0\}$ and $g_2,2/\sqrt{2} = \{1,−1,2\}$ were picked based on Slater-Koster s-d overlaps [59]. The phase diagram of $H$ was obtained as function of $(\epsilon_B − \epsilon_{OX})/t_B$ and $\kappa/t_B$.

B. The slave rotor mean field approach for Ni

Within the slave rotor approach, $b_{a,r,\sigma}^\dagger = f_{a,r,\sigma}^\dagger e^{i\varphi_r}$ was introduced, with $n_r^\theta$ being conjugate to the phase and taking on integer eigenvalues. For electron occupancy 0, 1, 2, 3, 4 (including both orbitals and both spins of Ni or the B site), $n_r^\theta$ was set to take values 2, 1, 0, −1, −2. In order to recover the physical Hilbert space, the constraint $n_r^\theta + \sum_\alpha f_{a,r,\sigma}^\dagger f_{a,r,\sigma} = 2$ was imposed. In this formulation, the Hamiltonian took on the form $H = H_1 + H_2 + H_3 + H_4$ but with $H_1, H_2$ being modified to

\[
H_1 = \epsilon_B \sum_{r,\sigma,\alpha} f_{a,r,\sigma}^\dagger f_{a,r,\sigma} + \epsilon_A \sum_{r,\sigma,\alpha} a_{r+\Delta,\sigma}^\dagger a_{r+\Delta,\sigma} + \epsilon_{OX} \sum_{r,\sigma,\delta} \Psi_{r+\delta,\sigma}^\dagger \Psi_{r+\delta,\sigma} \tag{6}
\]

\[
H_2 = -t_B \sum_{r,\alpha,\delta} g_{a\delta}(f_{a,r,\sigma}^\dagger [\Psi_{r+\delta,\sigma}^\dagger \Psi_{r-\delta,\sigma} + \text{h.c.}] + \frac{U}{2} \sum_r (n_r^\theta − 2)^2 − \lambda \sum_r (n_r^\theta + \sum_\alpha f_{a,r,\sigma}^\dagger f_{a,r,\sigma}) \tag{7}
\]

where the last term in $H_2$ imposed the average constraint on $n_r^\theta$. As in standard slave rotor mean field theory [51–54], a product form for the ground state $|\Psi_{f,\vartheta,a,\ell}\rangle = |\Psi_f\rangle |\Psi_\vartheta\rangle |\Psi_a\rangle |\Psi_\ell\rangle$ was assumed. Under this, $H_2$ was splitted as $H_2^f + H_2^\theta$, where

\[
H_2^f = -\Phi t_{Ni} \sum_{r,\alpha,\delta} g_{a\delta}(f_{a,r,\sigma}^\dagger [\Psi_{r+\delta,\sigma}^\dagger \Psi_{r-\delta,\sigma} + \text{h.c.}]) \tag{8}
\]

\[
H_2^\theta = -\chi t_{Ni} \sum_r (\Psi_{f,\vartheta}^\dagger \Psi_{f,\vartheta}) + \frac{U}{2} \sum_r (n_r^\theta − 2)^2 − \mu_\theta \sum_r n_r^\theta \tag{9}
\]

where $\Phi = (e^{i\varphi_r})$, and $\chi = \sum_{\alpha,\delta,\sigma} g_{a\delta}(f_{a,r,\sigma}^\dagger \Psi_{r+\delta,\sigma})$ and $\mu_\theta$ is the rotor chemical potential. Note that $H_3$ and $H_4$ remained unchanged under this product state decomposition of the ground state wave function. As discussed below another chemical potential $\mu_a$, was also introduced for the rest of the Hamiltonian namely, $H_1 + H_2^f + H_3$.

C. Solution strategy

A given $\Phi$ was assumed for the spinon sector coupled to the Bi and oxygen sites ($H_1 + H_2^f + H_3$) at the start of the calculation. Then this Hamiltonian was diagonalized in real space in 3D (6 × 6 × 6 unit cells) for a fixed value of $\varphi$. The chemical potential, $\mu_a$, was adjusted to fix 9 electrons per ABO$_3$ unit cell (with a total of 12 states). From the eigenstates, average Ni (spinon) occupation per site was calculated. The rotor occupation was then determined using the above constraint equation $(n_r^\theta = 2 − \sum_\alpha g_{a\delta}(f_{a,r,\sigma}^\dagger f_{a,r,\sigma}))$. Then the interacting rotor Hamiltonian $H_2^\theta$ was solved within a single site mean field theory. For this the rotor Hilbert space was restricted to have a maximum occupation of 4 and $\mu_\theta$ was adjusted to fix the rotor occupation to the value determined from the constraint equation, as described above. Having solved for the rotor sector, $\Phi$ was recomputed and used for the spinon-Bi-O Hamiltonian in a self consistent loop. Finally, the calculation was repeated by varying $\varphi$ to determine the optimal $\varphi$ corresponding to the minimum (ground state) energy that also includes the elastic cost term $H_4$. One such value is indicated in the inset of Fig. 3(c) with a blue arrow.

Indicators for metal insulator transitions

For determining the metallic and insulating states at the Ni sublattice the rotor expectation value $\Phi$ was tracked as a function of $\varphi$. $\Phi$ should go to zero in the Mott phase and should have finite value in the metallic phase. To determine the metal insulator transition for the full lattice, the total and projected density of states (DOS) were also calculated.
FIG. 7. (Color online) (a) and (b) show the $\varphi$ dependency of rotor order parameter $\Phi$ and ground state energy difference $\delta E$ (between the $\varphi \neq 0$ and $\varphi = 0$ cases). $\Phi$ is seen to vanish at $\varphi = 0.18$ and indicates the onset of the Mott phase at the Ni sites. The minimum of $\delta E$ occurs at $\varphi = 0.55$ (the blue arrow) by which time the Ni is already in the Mott state. (c) The projected DOS for Bi, Ni and oxygen are shown as indicated.

**Density of states:** The projected DOS for the Bi and oxygen were calculated as follows:

$$N_a(\omega) = \sum_{\alpha, \sigma} \sum_{i_a} |\langle \zeta_{\alpha} | i_a, \sigma \rangle|^2 \delta(\omega - \epsilon_{\alpha})$$

Here $a = \text{Bi, Oxygen}$ and $i_a$ are the corresponding sites. $|\zeta_{\alpha}\rangle$ and $\epsilon_{\alpha}$ are the eigenvectors and eigenvalues of $H_1 + H_f^2 + H_3$. For the Ni projected DOS we start with the local (Ni) Matsubara (retarded) Green’s function, defined as follows:

$$G_{i}^{\text{Ni}}(i\omega_n) = -\int_{0}^{\beta} d\tau e^{i\omega_n \tau} \langle b_{i,\sigma}(\tau) b_{i,\sigma}^\dagger(0) \rangle = -\int_{0}^{\beta} d\tau e^{i\omega_n \tau} \langle f_{i,\sigma}(\tau) f_{i,\sigma}^\dagger(0) \rangle \langle e^{-i\theta_i(\tau)} e^{i\theta_i(0)} \rangle$$

The spinon correlator (averaged over the spin indices) is as follows:

$$\frac{1}{2} \sum_{\sigma} \langle f_{i,\sigma}(\tau) f_{i,\sigma}^\dagger(0) \rangle = \frac{1}{2} \sum_{\alpha, \sigma} |\langle \zeta_{\alpha} | i, \sigma \rangle|^2 (1 - n_F(\epsilon_{\alpha} - \mu_s)) e^{-\tau(\epsilon_{\alpha} - \mu_s)}$$

Here the sites $i \in N_i$ and the factor of $1/2$ is due to the spin averaging. $|\zeta_{\alpha}\rangle$ and $\epsilon_{\alpha}$ are the eigenvectors and eigenvalues of $H_1 + H_f^2 + H_3$ and The rotor correlator can be expressed as follows:

$$\langle e^{-i\theta_i(\tau)} e^{i\theta_i(0)} \rangle = \frac{1}{Z_\theta} \sum_{l,l'} e^{-\beta \xi_{l}} \langle l | e^{-i\theta_i} | l' \rangle \langle l' | e^{i\theta_i} | l \rangle e^{\tau(\xi_{l} - \xi_{l'})}$$

Here $\xi_l$ and $|l\rangle$ are the eigenvalues and eigenvectors of the rotor Hamiltonian. $Z_\theta$ is the rotor partition function defined as $\sum_{l} e^{-\beta \xi_{l}}$. Using these in Eq. (11), the $\tau$ integration was performed and then $i\omega_n$ was set to $\omega + i\eta$ to obtain $G^{\text{Ni}}(\omega)$. The Ni projected DOS was calculated from the imaginary part of $G^{\text{Ni}}(\omega)$.

**D. Hybridization wave assisted Mott transition**

In Fig. 7(a) and (b) in the supplementary material we have shown the evolution of the rotor order parameter $\Phi$ and $(\delta E)$, the difference between the $\varphi \neq 0$ and $\varphi = 0$ ground state energies, as a function of $\varphi$. The data is shown for the AP phase marked with star in Fig. 3 (a) in the main paper. In Fig. 7(a) the Mott transition is signified by $\Phi$ going to zero at $\varphi = 0.18$, and as mentioned in the main paper, is concomitant with the Ni site occupation becoming half filled (2 per Ni). For $U = 0$ eV it was found that, increasing $\varphi$ from zero caused the Ni occupation to go to 2 per site beyond a certain value of $\varphi$, however the total DOS remained gapless. On the other hand setting $\varphi$ to zero...
at large $U$, the total DOS also was found to remains gapless. This clearly brings out the fact that, while both $U$ and $\varphi$ are required to form the insulating phase, it is the hybridization wave that drives the Mott state on Ni by tuning the Ni valence to half filling. This in turn opens up a gap in the full system DOS.

As seen in panel (b), the optimal distortion for minimum energy occurs at $\varphi = 0.55$, when the Ni is already in the Mott state. This stabilizes the distorted insulator phase. The relation between $\varphi$ and the Bi-O bond distortion is discussed in the main text.

In Fig. 7(c) we have shown the projected DOS for Bi, Ni and oxygen for the same AP parameter point, as in panels (a) and (b). We see that lower end of the charge gap has dominant contribution from oxygen, while the upper end is composed mainly by Ni DOS. This shows that hole doping would occur in oxygen states while electron doping will happen in Ni $d$ states. This is in line with usual negative charge transfer insulators.