Unusual Mott transition associated with charge-order melting in BiNiO$_3$
under pressure

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We study the electronic structure, magnetic state, and phase stability of paramagnetic BiNiO$_3$ near a pressure-induced Mott insulator-to-metal transition (MIT) by employing a combination of density functional and dynamical mean-field theory. We obtain that BiNiO$_3$ exhibits an anomalous negative-charge-transfer insulating state, characterized by charge disproportionation of the Bi 6s states, with Ni$^{2+}$ ions. Upon a compression of the lattice volume by $\sim$4.8\%, BiNiO$_3$ is found to make a Mott MIT, accompanied by the change of crystal structure from triclinic $P\bar{1}$ to orthorhombic $Pbnm$. The pressure-induced MIT is associated with the melting of charge disproportionation of the Bi ions, caused by a charge transfer between the Bi 6s and O 2p states. The Ni sites remain to be Ni$^{2+}$ across the MIT, which is incompatible with the valence-skipping Ni$^{2+}$/Ni$^{3+}$ model. Our results suggest that the pressure-induced change of the crystal structure drives the MIT in BiNiO$_3$.

The Mott metal-insulator transition driven by correlation effects has been an outstanding problem in condensed matter physics over many decades \cite{1}. In recent years, increasing attention has been drawn to the rare earth nickelate perovskites RNiO$_3$ ($R = $ rare earth, $R^{3+}$) with a high oxidation state of nickel, Ni$^{3+}$ 3$d^\nu$ \cite{2-4}. RNiO$_3$ compounds (except for LaNiO$_3$) exhibit a sharp metal-insulator transition (MIT) upon cooling below $T_{\text{MIT}}$ \cite{5}. The phase transition is accompanied by a structural transformation from an orthorhombic ($Pbnm$, GdFeO$_3$-type) to monoclinic ($P2_1/n$) crystal structure, with a cooperative breathing distortion of NiO$_6$ octahedra \cite{6}.

Based on the Ni-O bond lengths analysis and X-ray absorption spectroscopy, a partial Ni$^{(3\pm 4)+}$ charge disproportionation of Ni ions was proposed to occur in the insulating RNiO$_3$ phases \cite{5,6}. By contrast, further electronic structure calculations explain the insulating state of RNiO$_3$ in terms of bond disproportionation, with alternating Ni ions which (nearly) adopt a Ni$^{2+}$ 3$d^\nu$ ($\text{Ni}^{2+}$ ions with local moments) and 3$d^\nu$ $L^2$ (nonmagnetic spin-singlet) electronic configuration ($L$ denotes a hole in the O 2p band) \cite{3,8,7}. The transition temperature $T_{\text{MIT}}$ is strongly related to the degree of structural distortion of RNiO$_3$, determined by the size of R-ions. With decrease of the R-ionic radius, the Ni-O-Ni bond angle, which determines the degree of overlapping of the Ni 3d and O 2p orbitals (and hence the Ni 3d bandwidth), becomes smaller and $T_{\text{MIT}}$ is increased. In accord with this, the least distorted LaNiO$_3$ is found to be a correlated metal \cite{5,2}. In this context, the replacement of La$^{3+}$ with a larger ion, such as Bi$^{3+}$, should in principle result in a metal with (nearly) cubic perovskite structure. By contrast, BiNiO$_3$ has been found to be an insulator with a highly distorted perovskite structure (triclinic, $P\bar{1}$) and unusual valence ordering of the A-site Bi ions \cite{1}. In particular, based on X-ray and neutron diffraction, it was proposed that Ni ions adopt a Ni$^{2+}$ state, with an electronic configuration Bi$^{3+}$Bi$^{5+}$Ni$^{2+}$O$_3$ \cite{11,12}.

BiNiO$_3$ is known due to its colossal negative thermal expansion across the pressure-induced MIT, as suggested by a Bi/Ni charge transfer \cite{13}. Under ambient conditions, BiNiO$_3$ crystallizes in a triclinic perovskite crystal structure (space group $P\bar{1}$, a subgroup of $P2_1/n$) with two inequivalent Bi and four Ni sites \cite{11} (see Supplementary Fig. S1 \cite{14} and Ref. \cite{12} therein). It is an insulator with an energy gap of 0.68 eV \cite{1}. Below the Néel temperature of $T_N \sim 300$ K, BiNiO$_3$ is a G-type antiferromagnet with a near-antiferromagnetic alignment of Ni$^{2+}$ $S = 1$ spins, implying a predominant role of the antiferromagnetic Ni-O-Ni superexchange \cite{1,11,16}. Moreover, similarly to the small R-ions RNiO$_3$ the (charge-disproportionated) paramagnetic insulating phase of BiNiO$_3$ extends well above $T_N$, implying the crucial importance of correlation effects \cite{3,8,17}. BiNiO$_3$ shows a Mott insulator-to-metal phase transition (in the paramagnetic phase) under pressure (above $\sim$4 GPa) or upon substitution of the A-site Bi ions with La \cite{10,18}. In close similarity to RNiO$_3$, the MIT is accompanied by the change of crystal structure from the triclinic $P\bar{1}$ (insulating) to orthorhombic GdFeO$_3$-type $Pbnm$ (metallic) phase, with a volume collapse of $\sim$3\% and melting of charge disproportionation (Ni and Bi sites are equivalent in the $Pbnm$ phase of BiNiO$_3$). Based on the powder X-ray absorption and neutron diffraction, it was proposed that the melting of charge disproportionation leads to a charge transfer from Ni$^{2+}$ to Bi$^{3+}$, so that the electronic state of the $Pbnm$ metallic phase can be described as Bi$^{3+}$Ni$^{3+}$O$_3$ \cite{11,20}. This valence distribution however is in odd with photoemission spectroscopy results for $Pbnm$ BiNiO$_3$ that reveal that the nickel valence is far from being Ni$^{3+}$ \cite{10}.

The electronic properties of BiNiO$_3$ have recently been calculated using band-structure methods supplemented with the on-site Coulomb correlations for the Ni 3d states within density-functional theory (DFT)+U \cite{21} and dynamical mean-field theory (DMFT) \cite{22} methods \cite{23}.
However, these studies have mostly been focused on the valence skipping model, with a valence transition between the charge-ordered insulating \([\text{Bi}^{3\text{+}}\text{Bi}^{2\text{.5}+}\text{O}_{2\text{.5}}]\)[Ni\(^{2\text{+}}\)] and the uniform metallic \([\text{Bi}^{3\text{+}}][\text{Ni}^{3\text{+}}]\) state, assuming a long-range magnetic ordering. In fact, however, the MIT transition in BiNiO\(_3\) is known to occur in the paramagnetic state, implying the importance of electronic correlations. Moreover, a recent electronic structure study of BiNiO\(_3\) using DFT and slave rotor methods suggests that BiNiO\(_3\) is a self-doped Mott insulator [24].

In this paper, we explore the evolution of the electronic structure, magnetic state, and phase stability of paramagnetic BiNiO\(_3\) near the pressure-induced Mott MIT. We employ a fully self-consistent in charge density DFT+DMFT approach [24] implemented with plane-wave pseudopotentials [3, 4] which makes it possible to capture all generic aspects of the interplay between the electronic correlations, magnetic states, and crystal structure of BiNiO\(_3\) near the Mott MIT [28]. The DFT+DMFT calculations explicitly include the Bi 6s, O 2p, and Ni 3d valence states, by constructing a basis set of atomic-centered Wannier functions within the energy window spanned by the s-p-d band complex [29]. This allows us to take into account a charge transfer between the Bi 6s, O 2p, and Ni 3d states, accompanied by the strong on-site Coulomb correlations of the Ni 3d electrons. We use the continuous-time hybridization-expansion (segment) quantum Monte-Carlo algorithm in order to solve the realistic many-body problem [2]. We take the average Hubbard \(U = 6\) eV and Hund’s exchange \(J = 0.95\) eV as estimated previously for RNiO\(_3\) [8, 9]. We use the fully localized double-counting correction, evaluated from the self-consistently determined local occupations, to account for the electronic interactions already described by DFT.

In Fig. 1 we display our DFT+DMFT results for the phase equilibrium and local magnetic moments of Ni ions of paramagnetic BiNiO\(_3\). In these calculations, we adopt the crystal structure data for the ambient pressure triclinic \(P\bar{1}\) and high-pressure orthorhombic \(P\bar{bnm}\) structures (taken at a pressure of \(\sim \)7.7 GPa) from experiment [11], and evaluate the DFT+DMFT total energies as a function of lattice volume. Overall, our results for the electronic structure and lattice properties of BiNiO\(_3\) agree well with experimental data [10-13]. In particular, the triclinic \(P\bar{1}\) phase is found to be thermodynamically stable at ambient pressure, with a total-energy difference between the ambient-pressure and high-pressure phases of \(\sim \)160 meV/f.u.. The calculated equilibrium lattice volume \(V_0 = 248.8\) \(\text{Å}^3\) and bulk modulus \(K_0 = 149\) GPa (\(K' = \frac{dK}{dP}\) is fixed to \(K' = 4\)). Interestingly, all the Ni sites (the insulating \(P\bar{1}\) phase has four inequivalent Ni sites) are nearly equivalent and are in the Ni\(^{2\text{+}}\) state. The Ni\(^{2\text{+}}\) state is also confirmed by the eigenvalues analysis of the reduced Ni 3d density matrix, which suggests that the Ni ions are in the \(\sqrt{0.63}\langle d^8\rangle + \sqrt{0.32}\langle d^6\rangle\) state (all the rest contributions are below 0.05). Moreover, the calculated local (instantaneous) magnetic moment \(\sqrt{\langle m_z^2\rangle} \approx 1.67\) \(\mu_B\), agrees with the high-spin \(S = 1\) state of the Ni\(^{2\text{+}}\) ions.

Our calculations for the insulating \(P\bar{1}\) phase of BiNiO\(_3\) give a self-doped Mott insulator [31] with an energy gap of \(\sim \)0.3 eV (see the left panel of Fig. 2), in agreement with the resistivity and photoemission experiments [1] [10] (see also Supplementary Fig. S3). In particular, the energy gap lies between the occupied and unoccupied Ni \(e_g\) states, strongly mixed with the O 2p and the empty Bi2 6s states (the Bi1 6s states are fully occupied). The O 2p states are about -3.6 eV below the Fermi level, but have a substantial contribution both above and below \(E_F\). The latter is due to the strongly covalent B 6s–O 2p bonding, suggesting creation of a ligand hole caused by a charge transfer between Bi 6s and O 2p. While the occupied Bi1 and Bi2 6s states are seen to be localized deep below \(E_F\), at about -10 eV, the empty Bi2 6s states appear right at the bottom of the conduction band, with a sharp resonant peak at \(\sim \)0.4 eV. The top of the valence band has a mixed Ni 3d and O 2p character, with a resonant peak in the filled \(e_g\) bands located at about -0.4 eV below the Fermi level, which can be ascribed to the formation of a Zhang-Rice bound state [32].

Our result for the insulating \(P\bar{1}\) phase is characterized by a remarkable charge disproportionation of the Bi 6s states (due to the appearance of two different Bi sites with sufficiently different oxygen environment in the insulating phase). In fact, while the Bi1 6s states are almost completely occupied, the Bi2 6s Wannier occupancy is only about 1.56. This implies a
The Bi-ion radius of 1.31 Å, a typical value for the Bi


cel volumes at a temperature \( T = 387 \text{ K} \).

The crystal field levels of the Ni \( e_g \), O 2\( p \), and Bi 6s states under pressure (see Fig. 3). In fact, the O 2\( p \) levels are found to shift deep below the Ni \( e_g \) states under pressure, whereas the Bi 6s states go up in energy. The change of the O 2\( p \) and Bi 6s crystal field levels leads to the enhancement of the Bi 6s-O 2\( p \) hybridization under pressure, supporting the hybridization-switching mechanism proposed by Paul et al. [24]. Our results suggest that the PI-structured BiNiO\(_3\) is an unconventional Mott insulator in which the correlated insulating state is in much respect controlled by an \( s-p \) level splitting between the uncorrelated \( A \)-site Bi 6s and ligand O 2\( p \) states.

Upon further compression the PI-structured BiNiO\(_3\) becomes metallic below \( \sim 0.5 V_0 \), with the (instantaneous) local moment of \( \sim 1.36 \mu_B \). The MIT is accompanied with a collapse of local moments due to delocalization of the Ni 3\( d \) electrons, as seen from the be-
behavior of local spin susceptibility $\chi(\tau) = \langle \hat{n}_z(\tau)\hat{n}_z(0) \rangle$ (see Fig. 3). In fact, $\chi(\tau)$ is seen to decay fast with the imaginary time $\tau$. In agreement with this, the fluctuating moment is only of $\sim 0.75 \ \mu_B$ (evaluated as $m_{loc} = \int_0^{T/2} \chi(\tau)d\tau^{1/2}$), that differs sufficiently from the instantaneous moment. While the Bi 6s charge disproportionation is large in the highly-compressed metallic $P1$ phase, $\Delta N_{\text{Bi-6s}} \sim 1.04$, this suggests that the Bi 6s charge ordering alone cannot explain the insulating state of BiNiO$_3$. In agreement with this, our results for structural optimization of the $P1$ phase within nonmagnetic DFT give a metal with no evidence for the Bi 6s charge disproportionation (all the Bi sites are found to have nearly same oxygen environment), implying the crucial importance of strong localization of the Ni 3d electrons due to correlation effects.

Most importantly, our DFT+DMFT results provide a clear evidence that BiNiO$_3$ undergoes a structural transition from the triclinic insulating $P1$ to orthorhombic metallic $Pbnm$ structure below $\sim 0.95 V_0$ (above 8 GPa), in agreement with experiment. We found that the transition pressure depends very sensitively on the choice of the Hubbard $U$ value, with $P_c \simeq 1$ GPa and 15 GPa for $U = 5$ eV and 8 eV, respectively. The calculated bulk modulus ($U = 6$ eV) is $K_0 \approx 143$ GPa, i.e., $K_0$ is found to decrease by $\sim 4\%$ upon the MIT into the metallic state. The latter is rather uncommon for a Mott MIT, indicating the importance of lattice effects at the MIT in BiNiO$_3$.

The $Pbnm$ phase of BiNiO$_3$ is a correlated metal, characterized by a Fermi-liquid-like behavior with a weak damping of quasiparticles at the Fermi energy and by a substantial mass renormalization of $m^{\ast}/m \sim 2.5$ of the Ni $e_g$ bands. The Ni $e_g$ states show a quasiparticle peak at the Fermi level, with the upper Hubbard band at $\sim 1.0$ eV (see Fig. 2 and Supplementary Fig. S3). The calculated Ni-ion local magnetic moment of $1.3 \mu_B$ differs sufficiently from the fluctuating one $\sim 0.5 \mu_B$, implying delocalization of the Ni 3d electrons at the transition. Indeed, our result for the local susceptibility shows itinerant-moment-like behavior, similar to that of the highly-pressurized $P1$ phase (see Fig. 3). The $Pbnm$ phase is found to be metallic for all studied here unit cell volumes, as well as even for a large Hubbard $U = 12$ eV. The pressure-induced MIT is found to be accompanied by a collapse of the lattice volume by $\sim 5.2\%$, resulting in the melting of charge disproportionation of the Bi sites. Thus, in the $Pbnm$ phase all the Bi sites are equivalent, whereas the Bi 6s states are fully occupied, i.e., Bi$^{3+}$. Moreover, our analysis of eigenvalues of the reduced Ni 3d density matrix suggests that the Ni sites are in a Ni$^{2+}$ state, with an atomic configuration $\sim \sqrt{0.56|d^3| + \sqrt{0.30|d^5|}}$. We also notice a minor, below $\sim 10\%$, contribution due to the $d^6$ atomic state, $\sqrt{0.09|d^7|}$. Based on this result, we conclude that no change of the valence state of the Ni$^{2+}$ ions occurs across the pressure-induced MIT in BiNiO$_3$, i.e., the Ni$^{2+}$ state remains stable. The latter is in a sharp contrast with the valence skipping Bi/Ni model proposed earlier for BiNiO$_3$. Our results suggest a novel microscopic mechanism of a Mott MIT under pressure which is controlled by a charge-transfer between the A-site Bi 6s and ligand O 2p states. The pressure-induced MIT in BiNiO$_3$ is accompanied by a transition from the charge-disproportionated $\text{Bi}_2^{3+}(\text{Bi}_2^{2+}+\frac{L^2}{2}-\delta)_{0.5}$ to the charge-uniform $\text{Bi}^{3+}\frac{L^2}{2}$ valence state. The Bi 6s charge disproportionation (in the insulating $P1$ phase) occurs together with the MIT, which follows rather than produces the structural transition. We therefore conclude that the pressure-induced MIT and the concomitant melting of the Bi 6s charge ordering in BiNiO$_3$ is driven by the crystal structure transition. The latter highlights the complex interplay between the electronic structure and lattice effects in the vicinity of a Mott MIT in RNiO$_3$ nickelates.

In conclusion, we employed the DFT+DMFT approach to determine the electronic structure and phase stability of paramagnetic BiNiO$_3$ across the pressure-induced Mott MIT. Our results for the $P1$-structured BiNiO$_3$ under pressure propose a new mechanism for a correlation-driven metal-insulator transition, in which the Mott insulating state is (in much respect) controlled by the s-p level splitting between the uncorrelated A-site Bi 6s and O 2p states. We show that the pressure-induced MIT in BiNiO$_3$ is associated with the melting of charge disproportionation of the Bi ions and is accompanied by delocalization of the Ni 3d electrons. The phase transition results in a charge transfer between the Bi 6s and O 2p states, while the Ni sites remain to be Ni$^{2+}$. Our results suggest that the pressure-induced change of the crystal structure determines the MIT in BiNiO$_3$. We argue that the RNiO$_3$ compounds (with $R$ = rare earth and Bi) obey an intrinsic instability driven by the interplay of electron correlations and lattice effects, depending on the $R$-ion radius. It is associated with a crossover from charge disproportionation of the perovskite $B$-site Ni ions (realized for the $R$-ions with the ionic radii smaller

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**FIG. 4:** (Color online) Local spin correlation function $\chi(\tau) = \langle \hat{n}_z(\tau)\hat{n}_z(0) \rangle$ of the Ni 3d states calculated by DFT+DMFT for the ambient-pressure $P1$ (AP) and the high-pressure $Pbnm$ (HP) structures of BiNiO$_3$ for different volumes.
than that of La) to that of the A-site $R$-ions (for large $R$-ions), with LaNiO$_3$ being in between.

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[35] The crystal field levels for the Ni \( e_g \) states taken here as a reference energy are evaluated from the first moments of the interacting lattice Green’s function as \( \Delta_{\text{cf}} \equiv \text{diag}([\Sigma_k H_{\text{DFT}}^D(k)] + \text{Re}[\Sigma(i\omega_n \to \infty)]) \). Here, \( H_{\text{DFT}}^D(k) \) is the effective low-energy \( s-p-d \) Hamiltonian in the Wannier basis set. \( \Sigma(i\omega_n \to \infty) \) is a static Hartree contribution from self-energy \( \Sigma(i\omega_n) \).
Supplemental Material

Under ambient pressure, BiNiO$_3$ adopts a highly distorted perovskite (triclinic) crystal structure with space group $P\overline{1}$ (see Supplementary Fig. S1). It has two inequivalent Bi and four Ni sites and is characterized by the cooperative breathing Bi-O distortions of the lattice. The Bi sites are arranged in chains along the c axis, with a checkerboard pattern in the ab-plane. The $P\overline{1}$-structured BiNiO$_3$ is an insulator with an energy gap of $\sim 0.68$ eV as estimated from the electrical resistivity [1].

Under pressure above $\sim 4$ GPa, BiNiO$_3$ undergoes a structural transformation to the orthorhombic GdFeO$_3$-type ($Pbnm$) crystal structure, which has a single type of Bi and Ni ions. The phase transition is accompanied by a Mott insulator-to-metal transition and is associated with suppression of the breathing distortions of the lattice (all the Ni and Bi sites become equivalent in the $Pbnm$ phase).

Here, we employed the DFT+DMFT approach to explore the electronic properties and phase stability of para-magnetic BiNiO$_3$ under pressure using the DFT+DMFT method [2] implemented with plane-wave pseudopotentials [3, 4]. We start by constructing the effective low-energy Hamiltonian $\hat{H}_{\text{DFT}}$ (k), which explicitly contains the Bi 6$s$, Ni 3$d$, and O 2$p$ valence states, using the projection onto Wannier functions [5]. For this purpose, for the partially filled Bi 6$s$, Ni 3$d$, and O 2$p$ orbitals we construct a basis set of atomic-centered symmetry-constrained Wannier functions [6]. The Wannier functions are constructed over the full energy range spanned by the $s$-$p$-$d$ band complex using the scheme of Ref. [6]. We obtain the $s$-$p$-$d$ Hubbard Hamiltonian (in the density-density approximation)

$$\hat{H} = \sum_{k,\sigma} \hat{H}^{\text{DFT}}_{\sigma,\alpha\beta}(k) + \frac{1}{2} \sum_{i,\sigma'\alpha'\beta'} U_{\sigma\sigma'} \hat{n}_{i,\sigma\alpha} \hat{n}_{i,\beta'\sigma'} - \hat{H}_{\text{DC}},$$

where $\hat{n}_{i,\sigma\alpha}$ is the occupation number operator for the $i$-th Ni site with spin $\sigma$ and (diagonal) orbital indices $\alpha$. In Supplementary Fig. S2 we show our results for the band structure of BiNiO$_3$ calculated within nonmagnetic DFT in comparison with the Wannier Bi 6$s$, Ni 3$d$, and O 2$p$ band structure for the ambient-pressure $P\overline{1}$ and high-pressure $Pbnm$ phases of BiNiO$_3$. Our results for the leading Wannier hopping integrals between the Bi 6$s$ and neighbor ions in the ambient-pressure $P\overline{1}$ and high-pressure $Pbnm$ phases of BiNiO$_3$ are summarized in Table S1. All the calculations are performed in the local basis set determined by diagonalization of the corresponding Ni 3$d$ occupation matrices.

In order to solve the realistic many-body problem, we employ the continuous-time hybridization-expansion quantum Monte-Carlo algorithm [7]. The Coulomb interaction has been treated in the density-density approximation. The elements of the $U$ matrix are parametrized by the average Coulomb interaction $U$ and Hund’s exchange $J$ for the Ni 3$d$ shell. For all the structural phases considered here we have used the same $U = 6$ eV and $J = 0.95$ eV values as was estimated previously for RNiO$_3$ [8, 9]. The spin-orbit coupling was neglected in these calculations. Moreover, the $U$ and $J$ values are assumed to remain constant upon variation of the lattice volume. We employ the fully localized double-counting correction, evaluated from the self-consistently determined local occupations, to account for the electronic interactions already described by DFT, $\hat{H}_{\text{DC}} = U(N - \frac{1}{2}) - J(N_{\uparrow} - \frac{1}{2})$, where $N_{\uparrow}$ is the total Ni 3$d$ occupation with spin $\sigma$ and $N$ is the total occupation. Here, we employ a fully self-consistent in charge density DFT+DMFT scheme in order to take into account the effect of charge redistribution caused by electronic correlations and electron-lattice coupling.

In Supplementary Fig. S3 we show the spectral functions of paramagnetic BiNiO$_3$ calculated by DFT+DMFT in comparison with photoemission (PES) and X-ray absorption (XAS) spectra taken at room temperature [10]. Our calculations are performed in the paramagnetic state at a temperature $T = 387$ K, above the Néel temperature $T_N \sim 300$ K. To calculate the spectral functions, we employ the Padé analytical continuation procedure for the self-energy. In our calculations we adopt the experimental crystal structure data (atomic positions for the orthorhombic phase are taken from the experiment at a pressure of $\sim 7.7$ GPa [11]).

The calculated spectral functions are in overall good agreement with the experimental spectra. In particular, in the insulating triclinic phase, the energy gap lies between the occupied and unoccupied Ni $e_g$ states, strongly mixed with the O 2$p$ and the empty Bi2 6$s$ states (the Bi1 6$s$ states are fully occupied). Our results indicate that all the Ni sites (the insulating $P\overline{1}$ phase has four inequivalent Ni sites) are nearly equivalent. A sharp peak at about $-1.5$ eV originates from the occupied Ni $t_{2g}$ states, which form a lower Hubbard band at $-9$ eV. The PES spectral weight lying at about $-3$ and $-5$ eV is mainly due to the O 2$p$ states, the hump at $-10$ eV is predominantly due to the Bi 6$s$ states. In the metallic orthorhombic phase, the peak at the Fermi level and the spectral weight at the bottom of the conduction band are predominantly formed by the Ni $e_g$ and O 2$p$ states. The Ni $e_g$ upper Hubbard band appears at $\sim 1.0$ eV. The peak at about $-1.5$ eV is due to the occupied Ni $t_{2g}$ states. In contrast to the insulating phase, all the Bi states are occupied and are located at about $-10$ eV.

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TABLE S1: Leading Wannier hopping integrals (in meV) between Bi 6s and neighbor ions in the ambient-pressure P1̅ (left part) and high-pressure Pbnn (right part) phases of BiNiO₄.

| Atom Atom Distance (a.u.) | Hoppings (meV) | Atom Atom Distance (a.u.) | Hoppings (meV) |
|---------------------------|---------------|---------------------------|---------------|
| Bi 6s O 2p                | -1304, -1234, -71 | Bi 6s O 2p                | 0, 1709, 242  |
| Bi 6s O 2p                | -1410, 1037, 631 | Bi 6s O 2p                | -271, -1536, 95 |
| Bi 6s O 2p                | -280, -404, 1086 | Bi 6s O 2p                | -271, -1536, -95 |
| Bi 6s O 2p                | 772, 295, 1144  | Bi 6s O 2p                | 0, 622, 1132  |
| Bi 6s O 2p                | -674, 72, 839   | Bi 6s O 2p                | -69, -103, 957|
| Bi 6s O 2p                | 422, 47, -916   | Bi 6s O 2p                | -69, -103, -957|
| Bi 6s O 2p                | 052, -80, -757  | Bi 6s O 2p                | 6, -142, 935  |
| Bi 6s O 2p                | -385, 78, 204   | Bi 6s O 2p                | 6, -142, -935 |
| Bi 6s Ni e₉                | 6.03, 41, 2     | Bi 6s O 2p                | 0, -298, -151 |
| Bi 6s Ni e₉                | -37, 75, 163    | Bi 6s Ni e₉                | -49, -330     |
| Bi 6s Ni e₉                | -7, 58          | Bi 6s Ni e₉                | -6, -11       |
| Bi 6s Ni e₉                | 31, -126, -142  | Bi 6s Ni e₉                | 40, -12, 227  |
| Bi 6s Ni e₉                | 11, 48          | Bi 6s Ni e₉                | 6, 11         |
| Bi 6s Ni e₉                | -2, -274, -163  | Bi 6s Ni e₉                | 40, -12, 227  |
| Bi 6s Ni e₉                | 40, 12          | Bi 6s Ni e₉                | 0, -40        |
| Bi 6s Ni e₉                | 58, -14, 64     | Bi 6s Ni e₉                | 38, 156, -55  |

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**FIG. S1:** (Color online) Crystal structure of the triclinic $P\overline{1}$ (left) and highly-pressurized orthorhombic $Pbnm$ (right) phases of BiNiO$_3$. The oxygen atoms are depicted by small red balls. The figure was prepared with the VESTA program [12].

**FIG. S2:** (Color online). Band structure of BiNiO$_3$ calculated within nonmagnetic DFT for the ambient-pressure $P\overline{1}$ (left panel) and high-pressure $Pbnm$ (right panel) phases in comparison with the Wannier bands corresponding to the constructed Bi 6$s$, Ni 3$d$, and O 2$p$ Wannier functions (red dashed lines). The Fermi level is at zero energy.

**FIG. S3:** (Color online). Orbitally-resolved spectral functions of paramagnetic BiNiO$_3$ calculated within DFT+DMFT for the ambient-pressure $P\overline{1}$ (left panel) and high-pressure $Pbnm$ (right panel) phases of BiNiO$_3$. Photoemission (PES) and X-ray absorption (XAS) spectra are shown for comparison [10]. The DFT+DMFT calculations are performed at a temperature $T = 387$ K (above $T_N \sim 300$ K). The Fermi level is at zero energy.