Abstract

The unique properties of massless Dirac fermions lead to many remarkable phenomena, and a major challenge towards their technological exploitation is the development of materials with tunable Dirac states. Here we show that this goal may be achieved by using electron-electron correlations in the quasi 2D system BaNiS$_2$. By means of ARPES and first-principles calculations, we unveil the formation of Dirac states by the hybridization of correlated $d$-electrons with ligand orbitals, which provides an effective band crossing in the presence of a nonsymmorphic symmetry. We show that this mechanism forms Dirac cones extending over a wide energy window around the Fermi level, and that node location in $k$-space can vary along the $\Gamma - M$ symmetry line, instead of being pinned at symmetry points as commonly found in graphene and other Dirac materials. These unique characteristics make BaNiS$_2$ an ideal playground to explore electronic correlation effects in Dirac materials.

The topological classification of materials has been a major breakthrough in condensed matter physics as it explains some remarkable material properties simply through a band structure analysis. A key role is played by the band inversion mechanism: a parity twist of the Bloch states along a path through the inversion point in momentum ($k$-) space. The band inversion entails the existence of crossing points, such as Dirac nodes, when both time reversal and inversion symmetries are present in the system. Thus, Dirac states can emerge at the boundary between trivial insulators and topological insulators with inverted bandgap.

In the quest for Dirac materials and topological insulators, two main mechanisms have been hitherto followed. One is based on a strong spin-orbit coupling (SOC), while the other relies on symmetry-enforced degeneracies. In both cases, the choice of candidate materials is limited either by the chemistry or by the crystal symmetry. In this paper, we demonstrate a further band inversion mechanism in the quasi 2D system BaNiS$_2$, featuring a simple nonsymmorphic tetragonal $P4/nmm$ structure (Fig. 1a) characterized by a square lattice of S atoms. By means of angle resolved photoemission spectroscopy (ARPES) and first-principles calculations, we show the presence of Dirac cones at the Fermi level with predominant nickel $d$-orbital character, which arise from a band inversion due to the strong hybridization of the $d$-orbitals with the sulfur ligand $p$-orbitals, combined with the nonsymmporphic symmetry (Fig. 1b).

The Dirac nodes lie on the $\sigma_d$ reflection planes and extend along the $k_z$ direction piercing the whole Brillouin zone (BZ). By symmetry, there are four replicas of the line nodes, one per BZ quadrant. This is quite different from other topological node-line semimetals known to date, like Cu$_2$NPd [18] Ca$_3$P$_2$ [21] and ZrSiS [22] where the nodal lines are circles developing around high-symmetry points.

A relevant feature of the Dirac states in BaNiS$_2$ is the dominant $d$-orbital character. These states are sensitive to electronic correlation effects, a possibility which is rarely found in known Dirac semimetals that have been experimentally established. A demonstration of this is that the substituted compound...
BaCo$_{1-x}$Ni$_x$S$_2$ displays a metal-insulator transition (MIT) at a critical substitution level, $x_{cr} \sim 0.2$\cite{25,26}, where the Co-rich side is an antiferromagnetic insulator. This MIT is of particular interest because it is exclusively driven by electron-electron correlation and is associated with a competition between an insulating antiferromagnetic phase and an unconventional paramagnetic metal\cite{25,26}. The $d$-orbital correlated Dirac fermions may give rise to novel ways of realizing electronic or topological states. This has only recently been studied in the rare case of kagome magnetic structure\cite{27,28}, while in other weakly correlated Dirac materials studied so far, the band inversion mechanism and topological phases are mainly controlled by $p$-orbitals\cite{29}. Furthermore, the effort to generate correlated Dirac fermions has only been possible by radically altering the crystal structure, e.g. by twisting bilayers of graphene\cite{30,31}.

Overall, in this paper we show that BaNiS$_2$ hosts a novel band inversion mechanism allowing to study the interplay of Dirac and correlated $d$-electrons physics. For instance, we envisage that the strength of the electron-electron correlations controlled by the Co/Ni substitution may be used to effectively tune the Dirac states and, more generally, the topological states. In order to explore this possibility, we develop a minimal tight-binding model derived from first principles that captures the essential features of the above-mentioned mechanism, thus enabling its application to a wide class of Dirac and topological materials.

1 Experimental observation and ab initio calculations of correlated Dirac states

Angle resolved photoemission spectroscopy. The electronic structure of BaNiS$_2$ was studied using ARPES on high-purity single crystals, grown by a self-flux method and previously characterized by X-ray diffraction. In Fig. 1(a) we represent a three dimensional ARPES map of the BZ for which the high symmetry directions are shown in Fig. 1(c). The top surface shows the constant energy contour at the Fermi level, below we report the band dispersion along the high symmetry directions $\Gamma - M$, $\Gamma - X$ and $X - M$. Along $\Gamma - M$, we observe linearly dispersing bands and gapless nodes at the Fermi level. The Fermi surface reveals two pairs of such Dirac-like crossings that are related to each other by the time-reversal and the $C_2$ operation symmetry of the $C_{2v}$, little group for the k-vectors along the $\Gamma - M$. We also observe a small electron pocket centered at the $\Gamma$ point, leading to the semi-metallic properties of BaNiS$_2$\cite{32,33}. In Fig. 1(b) we present the evolution of the bands versus the binding energy through constant energy contours in the $k_x - k_y$ plane. The electron pocket at $\Gamma$ disappears at $E \sim -0.14$ eV, and then evolves into a growing star-shaped dispersion as the binding energy increases. On the other hand, the linearly dispersing bands along $\Gamma - M$ remain isolated up to about $E \sim -0.35$ eV. Unlike graphene, these bands create an elliptical section on the constant energy maps near the Fermi level (Fig. 1(c)). This asymmetry arises from the tilted type-I nature of the Dirac cone, to be discussed below.

Henceforth, we focus on the linearly dispersing bands. In order to elucidate their $k_z$ dispersion, we performed a series of photon energy dependent measurements from 25 eV to 70 eV, which ensures a complete span of the BZ. In Fig. 2(d) we show the ARPES results at different photon energies. The slight variations of the intensity are the effect of the matrix elements. However, we observe no $k_z$ dispersion of the linear bands within the experimental resolution. The Dirac point always occurs at about 20 meV above the Fermi level and along the $\Gamma - M$ direction and the velocity of the bands does not change with $k_z$. These dispersionless features point at a 2D nature of the Dirac cones, which form straight lines along the $k_z$ direction. We estimate the Fermi velocity near the Dirac point to be about 2 eVÅ.

Ab initio electronic band structure calculations. In order to explain the experimental bands and, specifically, the orbital character of the Dirac states, we performed band structure calculations in the density functional theory (DFT) framework using a modified hybrid Heyd-Scuseria-Ernzerhof (HSE) functional with an optimised 7% of exact exchange, while keeping the regular screening length $\lambda \approx 4.8$ Å in the exchange potential.\cite{34,35} The hybrid functionals are nonlocal, orbital dependent and account for static non-local screened-exchange correlations relevant to reproduce quantum oscillations data.\cite{36,37} We included Ni spin-orbit (SO) interactions, which are important in BaNiS$_2$\cite{25}. In Fig. 3 we compare the DFT calculations with the ARPES data. The agreement is good, particularly at $k_z = 0$. The location and the shape of the Dirac cones are well reproduced along $\Gamma - M$ and $Z - A$ as well as the asymmetric tilted nature of the cones.

In accordance with recent DFT+U calculations\cite{38}, we ascribe the electronic states close to the Fermi level mainly to the Ni 3$d$-orbitals hybridized with the S 3$p$-orbitals. Hereafter, we consider a Cartesian reference frame where the $x$- and $y$-axis are parallel to the Ni-S bonds in the tetragonal $ab$-plane. Neighbouring Ni ions are aligned along the diagonal $xy$ direction (Fig. 1). In this frame, at the crossing points, located along the $(u, u, v)$ directions, the bands have dominant $d_{x^2-y^2}$ and $d_{z^2}$ character.

This multi-orbital nature was confirmed by a polarization dependent laser-ARPES study. Owing to the different parity of the $d$-orbitals with respect to the scattering plane of the experiment\cite{39}, the out-of-plane $d_{x^2}$ and the in-plane $d_{x^2-y^2}$ states are detectable with $p$ and $s$ polarization of the incident light, respectively. These results confirm the character of the Dirac bands near the Fermi level obtained from the orbital resolved HSE band structure (see Supplemental Materials).
2 Symmetry analysis of the Dirac states: proximity with an insulating topological phase

As reported in Fig. 1(a), the crystal structure of BaNiS$_2$ is made of square-lattice layers of staggered, edge-sharing NiS$_2$ pyramids, pointing along the out-of-plane [001] c-axis direction. The Ni atoms inside the S pyramids probe a crystal field that splits the atomic $d$-shell into the following levels (in descending energy order): $d_{x^2-z^2}$, $d_{xy}$, the degenerate doublet ($d_{xz}$, $d_{yz}$) and $d_{yz}$. Due to the $3d^84s^0$ electronic configuration of the Ni$^{2+}$ ion, we expect all $d$-orbitals to be filled, except the two highest ones, $d_{x^2-y^2}$ and $d_{z^2}$, which should be nearly half-filled if the Hund’s exchange dominates the crystal field splitting between them.

The puckering of the BaNiS$_2$ layers gives rise to a tetragonal nonsymmorphic $P4/nmm$ structure characterized by a horizontal gliding plane which generates two Ni (and apical S) positions at $(1/4,1/4,z)$ and $(3/4,3/4,−z)$, separated by a fractional $f=1/2,1/2,0$ translation in the plane, Fig. 1(b). The two Ni atoms occupy the Wyckoff position 2c, corresponding to the M point, while the two planar S are at the position 2a, which corresponds to the $\Gamma$ point.

At M, the energy hierarchy of the atomic orbitals follows closely the crystal field splitting (Fig. 1(a)). The little group admits the following four 2D irreducible representations $E_{M1}=\ldots=2\sum \gamma$ each originating from the same orbitals of the two inequivalent Ni. However, the levels stacking at M, whose little group is isomorphic to $D_{4h}$, differs from that predicted by the crystal field. This is due to the sizeable hybridization of Ni $d$-orbitals with the S $p$ ligands. Owing to the nonsymmorphic symmetry, each Bloch eigenfunction at $\Gamma$ is either even or odd upon exchanging the inequivalent Ni and S within each unit cell. Even and odd combinations of identical $d$-orbitals belonging to inequivalent Ni atoms split in energy since they hybridize differently with the ligands. The even combination of the $d_{x^2-y^2}$ Ni orbitals is weakly hybridized with the $p_z$-orbitals of the planar S, since the two Ni are out of the basal plane. On the other hand, the odd combination is non-bonding. It follows that the $B_{1g}$ even combination shifts up in energy with respect to the $B_{2g}$ odd one. Seemingly, the $A_{2u}$ odd combination of the $d_{x^2-y^2}$ orbitals hybridizes substantially with the $p_z$-orbitals of the planar and apical S, thus increasing substantially the energy of the odd combination. Eventually, this energy becomes larger than that of the $A_{1g}$ state, and even of the states made of even and odd combinations of the $d_{x^2-y^2}$-orbitals. This leads to a reverse of the crystal field order as reported in Fig. 1(b).

Because the irreps at the A and Z k-points are equivalent to those at M and $\Gamma$, respectively, the orbital hierarchy found at M and $\Gamma$ must be preserved along the $M−A$ and $\Gamma−Z$ directions. Thus, along the $(0,0,v)→(1/2,1/2,v)$ path, for any v, there must be a band inversion between bands with predominant $d_{x^2}$ and $d_{x^2-y^2}$ characters. Remarkably, a band crossing is allowed without SOC, and leads to two Dirac points, one right at the Fermi energy for $k_y=0$. Indeed, the crossing bands transform like different irreps of the little group, which is isomorphic to $C_{2v}$ for a k-point $(u,u,v)$ with $v=0,1/2$, and to $C_s$ with $v∈[0,1/2]$.

The inclusion of the SOC opens sizeable gaps in the band structure, as reported earlier. The protection of the crossing points against SOC can be determined by the double groups of the $C_{2v}$ and $C_s$ little groups. Since the related double groups have a single irreducible representation, the SOC can make all crossings avoided along $\Gamma−M$. Our ab initio HSE calculations show that the gap that opens between formerly crossing levels is weaker the closer the M point. In particular, the gap at the Dirac point close to the Fermi energy is as small as $\approx0.02$ eV, which is at the limit of our ARPES resolution (see Supplemental Materials).

Finally, a parity analysis of the band structure (Fig. 4(a)), unveils that BaNiS$_2$ is close to a weak $Z_2$ topological insulator because of the inverted band gap at $\Gamma$ between opposite parity $E_a$ and $B_{1g}$ states. Both states are however slightly below the Fermi level, so the system remains metallic with a small Fermi pocket centered at $\Gamma$, in agreement with the ARPES data.

3 A model Hamiltonian for $p-d$ hybridized Dirac states

Previous theoretical calculations have shown that the Bloch functions near the Fermi level have components on both the S $3p$ and the Ni $3d$-orbitals. Here we derive a low-energy model by generating the 22 Wannier orbitals of the whole $p-d$ manifolds from the HSE calculation without SOC. In fact, an accurate description of the Dirac cones can be already obtained by considering just the 10 Wannier orbitals deriving from $d_{xz}$ and $d_{yz}$ Ni orbitals, and the planar-sulfur $p$-orbitals (see Sec. 4). Exploiting the nonsymmorphic symmetry, we can further simplify the TB model into one with a unit cell containing a single Ni atom. Finally, assuming that the $p$-orbitals lie well below the Fermi level, we can integrate them out and obtain the following effective two-band Hamiltonian:

$$\hat{H}(\mathbf{k}) = \sum_{\alpha} \left( \hat{E}_{\alpha} - t_{\alpha} (\cos k_x + \cos k_y) \right) n_{\alpha\mathbf{k}} + \sum_{\sigma,a,b} t_{ab} \sin k_x \sin k_y \left( d_{a\sigma k}^\dagger d_{b\sigma k} + H.c. \right),$$

(1)
where the reference frame is rotated by 45° around the z-axis, so that the Ni-Ni bonds are now along the x- and y-axis and $d_{x^2-y^2} \rightarrow d_{xy}$. The orbital indices are now $a = z^2, xy$. The Hamiltonian parameters have an implicit dependence on $k_z$. In particular, at $k_z = 0$, they are as following in eV units: $E_{x^2} = -0.59$, $E_{xy} = 1.21$, $t_{x^2} = -0.59$, $t_{xy} = 0.90$, $t'_{x^2} = -0.57$, $t'_{xy} = 3.1$ and $t_{12} = 0.44$.

The effective hybridization among the two orbitals vanishes along $\Gamma \rightarrow X$ and along $\Gamma \rightarrow Y$, as dictated by symmetry. Moreover, because of the band inversion at $\Gamma$ with respect to the BZ boundaries, the $d_{x^2}$-band goes down ($t_{x^2} < 0$) whilst the $d_{xy}$-band goes up ($t_{xy} > 0$) moving away from $\Gamma$. It follows they should cross at points $k^* = (\pm k^*, 0)$, $(0, \pm k^*)$, where $k^* > 0$ is solution of an implicit equation that depends on the model parameters (see Sec. 5).

By expanding the effective model in Eq. 1 to linear order around the gapless points $k^*$, i.e., $k = k^* + \mathbf{q}$, we obtain a Dirac Hamiltonian of the form:

$$H^*(\mathbf{q}) \simeq \hat{h}_{0} q_{x} \mathbf{1} + \hat{h}_{x} q_{x} \sigma_{x} + \hat{h}_{y} q_{y} \sigma_{y}$$

where $\mathbf{1}$ is the identity matrix, $\sigma_{x,y,z}$ are the Pauli matrices, and all the coefficients are obtained by the parameters in Eq. 1. The opposite node, located at $k = (-k^*, 0)$, has opposite chirality. The remaining two nodes at $k = (0, \pm k^*)$ are obtained by the $C_{2v}$ symmetry. Note that Eq. 2 shows a non trivial k-dependence in the $\Gamma$ component, which implies an elliptical shape of the Dirac cone as shown in Fig. 5. This result matches the experimental observation discussed in Sec. 1. To highlight this feature, we compared in Fig. 5(a)-(b) the experimental and theoretical constant energy contours at the Fermi level and slightly below it. The theoretical results obtained with the effective Dirac model accurately reproduce the ARPES data and are applicable to other square-lattice systems with similar d-p hybridisation properties.

4 Alignment of the Dirac nodes with the Fermi level

Besides a strong d-p hybridization and their location at a generic position along $\Gamma - M$, rather than at any specific high-symmetry point, the Dirac bands of BaNiS$_2$ display a further unusual feature. Namely, the Dirac nodes are aligned with the Fermi level. This is a consequence of the Luttinger theorem applied to the particular d-levels energy hierarchy and to the atomic d-orbitals filling of BaNiS$_2$. The former is provided by the square-pyramidal crystal field splitting, implying that the two topmost energy levels in the d-manifold are of $z^2$ and $x^2 - y^2$ symmetries. The latter is given by the Ni electronic configuration, which leaves the $d_{x^2}$ and $d_{x^2-y^2}$ states with integer partial occupation: $2n_{x^2} + 2n_{x^2-y^2} = 4$, by counting both Ni in the unit cell, while the other d states are completely filled. Therefore, in the absence of other Fermi pockets, the $C_{2v}$-allowed crossing between the corresponding $d_{x^2}$ and $d_{x^2-y^2}$ bands must occur at the Fermi level. This condition is indeed nearly satisfied in BaNiS$_2$ owing to its semimetallic characteristics. Specifically, in addition to the Dirac points, the Fermi surface of BaNiS$_2$ is made only of very small cylindrical electron pockets centered along the $\Gamma - M$ direction, populated by electrons much less mobile than the Dirac ones. Thus, the Dirac points are weakly dispersive along the $k_z$ direction, with the Fermi level in the $[0 - 25]$ meV ($[0 - 75]$ meV) range from the crossing point energy, according to ARPES (HSE), as reported in Fig. 5(d). This leads to the formation of Dirac nodal lines.

In addition, thanks to the nonsymmetric shell of the Dirac fermions, the symmetry protected topological contacts are robust against on-site Coulomb interaction present. Should the Hubbard repulsion be strong enough, it could prevent the Dirac cone formation by Mott gap opening in a $2n_{x^2} = 2$, $2n_{x^2-y^2} = 2$ half-filled situation. However, the nonsymmetric shell implies a double degeneracy of the bands at M, i.e. $2n_{x^2} (k = M) = 4$, which breaks the filling condition for a Mott insulator.

5 Tunability of the Dirac states

The hybridization of correlated d electrons with ligand p-orbitals makes BaNiS$_2$ a model system to study Dirac fermions whose energy spectrum can be tuned by electron-electron interactions (see Methods). We envisage that the Dirac nodes can be moved along $\Gamma - M$ by tuning the $p - d$ hybridization amplitude (Fig. 5(c)) for instance, by means of chemical substitution in BaCo$_2$Ni$_{1-x}$S$_2$. Such movable Dirac nodes in the k-space have recently attracted a great deal of interest in the context of topological phase transition. For instance, their manipulation offers the possibility of turning a Dirac semimetal into an insulator. To the best of our knowledge this kind of transition has only been predicted or realized using optical lattices. The present system could be a first realization of such a physics in the solid state. Remarkably the same chemical substitution is responsible for the MIT in this system, since cobalt doping increases the strength of the electronic correlations. Controlling the shape and position of the Dirac cones is also expected using pressure or strain in thin films. Specifically, strain can be used to distort the underlying square lattice, thus breaking one of the symmetries that protect the fourfold occurrence of the Dirac nodal lines. Non-trivial phases, such as Weyl semimetals, could then be triggered by time-inversion breaking perturbations, like an external electromagnetic field. A further possibility is the
creation of spin-chiral edge states thanks to the proximity of the material to a topological insulator. We emphasize the generality of the present approach, which can be extended to a wide class of materials described by the $p - d$ effective Hamiltonian, to forge new Dirac states that can be tuned by electronic correlations.

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Data availability statement. The data supporting the findings of this study are available from the corresponding authors upon reasonable request.

6 Methods

ARPES measurements. Single crystals of BaNiS$_3$ were cleaved in situ, exposing the ab plane under UHV conditions (base pressure $10^{-11}$ mbar or better). The synchrotron radiation ARPES measurements were performed on the Advanced Photoelectric Effect (APE) beamline at the Elettra light source, with linearly polarized beam and different photon energies. The sample temperature was 70 K. The data were collected with a VG-DA30 Scienta hemispherical analyzer that operates in deflection mode and provides high-resolution two-dimensional $k$-space mapping while the sample geometry is fixed.

Ab initio calculations. We used the Quantum Espresso package to carry out ab initio DFT calculations. The geometry of the cell and the internal coordinates are taken from experiment. We replaced the core electrons of the Ni, Ba, and S atoms by norm-conserving pseudopotentials. The Ni pseudopotential is fully relativistic, with 10 valence electrons (4s$^2$3d$^8$) and nonlinear core corrections. The Ba pseudopotential includes the semicore states, while the S pseudopotential has 3s$^2$3p$^4$ in-valence electrons. We employed a 8 × 8 × 8 electron-momentum grid and a Methfessel-Paxton smearing of 0.01 Ry for the k-point integration. The plane-waves cutoff is 60 Ry for the wave function. The non-local exchange terms of the HSE functional are computed through the fast implementation of the exact Fock energy based on the adaptively compressed expression scheme. In the non-local Fock operator evaluation, the integration over the q-points is downsampled on a 8 × 8 × 2 grid. We applied a half-a-grid shift in the z direction to minimize the number of nonequivalent momenta in the k + q grid. By means of the WANNIER90 code, we performed a Wannier interpolation of the ab initio bands in the energy window spanned by the $p - d$ manifold, to accurately resolve the band structure, chemical potential, and Fermi surface, and to derive a minimal TB model.

Table 1: Left column: TB coefficients used in the low-energy 5 × 5 Hamiltonian Eq. as derived from a Wannier fitting of the ab initio HSE band structure. Right column: expression of the hybridization functions appearing in the same low-energy Hamiltonian.

| TB coeff. (eV) | Hybridization functions |
|---------------|-------------------------|
| $E_{x,y}$ = 6.33 | $\tilde{v}_{x,y} = \sin \frac{k_x}{2} \sin \frac{k_y}{2}$ |
| $E_{z}$ = 6.85 | $\tilde{v}_{z} = \cos \frac{k_x}{2} \cos \frac{k_y}{2}$ |
| $E_{z^2}$ = 7.48 | $\tilde{v}_{z^2} = 0.22 \tilde{v}_{x,z} = \cos \frac{k_x}{2} \cos \frac{k_y}{2} \cos \frac{k_z}{2}$ |
| $E_{z^2-y^2}$ = 7.54 | $\tilde{v}_{z^2-y^2} = 0.22 \tilde{v}_{y,z} = -\sin \frac{k_x}{2} \cos \frac{k_y}{2} \cos \frac{k_z}{2}$ |

Derivation of the Dirac Hamiltonian. We considered the TB Hamiltonian in terms of the Wannier orbitals for the $p-d$ manifolds. Starting from this Hamiltonian and considering only the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals from the Ni-atoms as well as the $p$-orbitals from the planar S we obtain a ten bands Hamiltonian. This model can be further simplified exploiting the crystalline structure to reduce the unit cell. Upon changing the sign of the $p_z$-orbital of one among the two S-atoms within each unit cell, neglecting SOC and keeping only nearest-neighbor Ni-S hopping terms, we can transform the TB Hamiltonian into a new one that is translationally invariant on a bipartite square lattice of halved unit cells, each containing just one Ni and one S.

We work in a reference frame obtained upon rotating the x-y plane by 45° around the z-axis, so that $d_{z^2-y^2} \rightarrow d_{xy}$, and Ni-directions are along either the x or y new axis. The resulting effective 5 × 5 Hamiltonian reads:

$H(k) = \sum_{i=x,y,z} E_i n_{ik} + \sum_{\alpha=x,z} E_{\alpha} n_{\alpha k} + \sum_{\alpha=x,z} \sum_{\sigma} v_{\alpha}(k) \left( d_{\alpha \sigma}^\dagger \tilde{v}_{\alpha \sigma} + H.c. \right)$, (3)

where $k = (k_x, k_y)$, $n_{ik}$ and $n_{\alpha k}$ are the occupation numbers in momentum space. The hybridization amplitudes have the form $v_{\alpha}(k) = t_{\alpha \sigma} \tilde{r}_{\alpha \sigma}(k)$. The parameters are compatible with the spatial symmetries and implicitly depend on $k_z$. The analysis is carried out here for $k_z = 0$. However, the residual $k_z$ dependence of the parameters is very weak, owing to the quasi-2D nature of the material. Their values and the expressions for $\tilde{r}_{\alpha \sigma}$ are reported in Table 1, where the hopping amplitudes are defined in terms of the TB model as:

$t_{z^2} = \gamma_{z^2}$, $t_{xy} = \gamma_{xy}$, $t_{z} = \eta_0 \gamma_{z^2}$, $t_{\alpha} = 2 \eta_0 \gamma_{\alpha \sigma}$, $t_{\alpha \beta} = \gamma_{\alpha \beta} \gamma_{xy} \gamma_{x^2-z^2} - \gamma_{xy} \gamma_{\alpha \beta} \gamma_{x^2-z^2}$, and $E_{\alpha} = E_{\alpha \sigma} - \gamma_{\alpha \sigma} - \gamma_{x^2-z^2}$, with the notation $\eta_0 = 2t_{\alpha \sigma} / \sqrt{E_{\alpha}}$ and $n_{\alpha \sigma} = \pm 1$ for $\alpha = x^2-y^2, xy$, respectively.

Denoting with $E_d, E_p$ the on-site energies of the $d$ and the $p$-orbitals,
we find that the charge transfer energy is positive $E_d - E_p > 0$. Thus, assuming that the $p$-orbitals lie well below the Fermi level, we can integrate them out in a functional integral formalism, to obtain a low-energy effective $2 \times 2$ Hamiltonian which describes the physics of the relevant $d$-orbitals near the Fermi level, Eq. 1. The Dirac Hamiltonian is determined by linearization of the effective model around the gapless nodes, which in turn are determined by the equation: $k^* = \cos^{-1} \left( \frac{Y}{D} \right)$, where $Y = \tilde{E}_d - \tilde{E}_p - \gamma_{zz}^2 + \gamma_{zxy}^2$ and $D = 2\gamma_{zz}^2 - \gamma_{zxy}^2 + \gamma_{xy}^2$. The resulting model parameters $\hat{h}_0 = -\frac{1}{2}(2\gamma_{zz}^2 - 2\gamma_{zxy}^2 - \gamma_{xy}^2 - \gamma_{zz}^2) \sin k^*$, $\hat{h}_x = (-\gamma_{zz} \gamma_{zxy}^2 + \gamma_{xy} \gamma_{xy} \gamma_{zxy}) \sin k^*$ and $\hat{h}_y = -\frac{1}{2}(2\gamma_{zz}^2 + 2\gamma_{zxy}^2 - \gamma_{zz}^2 + \gamma_{zxy}^2) \sin k^*$, which are expressed in terms of the TB coefficients of the $5 \times 5$ Hamiltonian.

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Figure 1: **Crystal structure and Brillouin zone.** (a) Crystal structure of BaNiS$_2$. Blue, red and yellow spheres represent the Ni, S and Ba atoms, respectively. The tetragonal unit cell is indicated by black solid lines. The lattice parameters are $a = 4.44$ Å and $c = 8.93$ Å. On the top the projection of the unit cell in the $xy$ plane, containing two Ni atoms is shown. (b) Left panel: Schematics of the $d$- and $p$-orbitals of Ni and S, respectively. Right panel: The strong hybridization of the $d$-orbitals with the ligand $p$-orbitals, favored by the non-symmorphic symmetry of the lattice, is responsible for the band inversion. (c) First Brillouin zone, and high-symmetry directions.
Figure 2: **Experimental electronic band structure.** (a) A three-dimensional ARPES map acquired with 70 eV photon energy. The top surface shows the Fermi surface and the sides of the cube present the band dispersion along the high symmetry directions depicted with the white arrows. The linearly dispersing bands along the $\Gamma - M$ cross each other at the Fermi level, creating four Dirac nodes on the Fermi surface. (b) Stacking plots of constant-energy contours show the band structure evolution with respect to the binding energy. In particular, we observe the ellipse-shaped section of the linearly dispersing bands on the $k_x - k_y$ plane that loses symmetry as the binding energy increases. (c) Elliptical section of the Dirac cone for the binding energy of 100 meV. The band dispersion along the small and big axis of the ellipse are also shown. (d) ARPES yield for the linearly dispersing bands, along $\Gamma - M$ and at different photon energies. The dashed blue lines are guides to the eyes.
Figure 3: **Band structure calculations.** Comparison between the electronic band structure calculations with the HSE functional and the experimental data acquired with 70 eV of photon energy.
Figure 4: **Band symmetries along the MΓ direction.** (a) Band symmetries along the MΓ direction. At the right (left) -hand side of the panel, we report the symmetries at Γ (M), while the symmetries in between follow the irreps of the $C_{2v}$ point group, represented by the color code in the key. The outer $+/−$ signs indicate the parity of the respective Bloch wave functions at the beginning and at the end of the k-path. (b) Evolution of the energy splitting between even and odd combinations of $d$-orbitals along MΓ. The dominant orbital character is reported. The red (dark-green) vertical arrows indicate the splitting $\Delta_3 (\Delta_1)$ between the $d_{x^2−y^2}$ ($d_{z^2}$) bands at Γ due to the hybridization with the ligand $p_z$-orbitals. The blue arrow is the splitting $\Delta_2$ of $d_{xz}/d_{yz}$ bands at Γ due to their hybridization with the $p_x/p_y$ orbitals.
Figure 5: **Tight-binding $p$-$d$ model and Dirac Hamiltonian.** (a)-(b) Constant energy contours at (left) and near (right) the Fermi level. Experimental data are reported in the top (a) panels. Theoretical calculation are obtained from the effective Dirac model (Eq. 2) and plotted in the original, i.e. non-rotated, basis. The comparison highlights the agreement between theory and experiments. The effective model explains the presence of elliptically shaped Dirac cones, as observed in ARPES measurements, along the $\Gamma - M$ direction. (c) Evolution of the electronic dispersion near the Dirac node in the $\Gamma - M$ direction of the original basis. The different lines are function of the hybridization among the $p$ and $d$ bands. The data are obtained from the model Hamiltonian (see Methods Eq. 3) with the substitution of $t_{i\alpha} \rightarrow t_{i\alpha} + g$, with $\alpha = z^2, xy, i = x, y, z$ and $g = 0.0, 0.2, 0.4, 0.6$.  

\[ E = E_f = 100 \text{ meV} \]