Electronic states in the gap of a superconductor inherit intriguing many-body properties from the superconductor. Here, we create these in-gap states by manipulating Cr atomic chains on the $\beta$-Bi$_2$Pd superconductor. We find that the topological properties of the in-gap states can greatly vary depending on the crafted spin chain. These systems make an ideal platform for non-trivial topological phases because of the large atom-superconductor interactions and the existence of a large Rashba coupling at the Bi-terminated surface. We study two spin chains, one with atoms two-lattice-parameter apart and one with square-root-of-two lattice parameters. Of these, only the second one is in a topologically non-trivial phase, in correspondence with the spin interactions for this geometry.

PACS numbers: 74.55.+V,74.78.-w,74.90.+n

I. INTRODUCTION

The scanning tunneling microscope (STM) permits unprecedented control at the atomic level. Since the early days of STM, atoms have been moved, unveiling matter on the atomic scale. Atoms involve interactions that can have a profound impact on the electronic properties of host substrates, as such, designing atomic structures can lead to creating new quantum states. Magnetic atoms strongly modify the low-energy electronic properties of superconductors. This is due to the appearance of in-gap states caused by the weakening of the Cooper-pair binding. These in-gap states are usually called Yudin-Shiba-Rusinov (YSR) states. Recently, the interest on in-gap states has increased due to the suggestion of topological edge states appearing on chains of magnetic impurities on superconductors. These zero-energy edge states imply the presence of a topological superconducting phase. The zero-energy edge states are Majorana bound states (MBS) with non-trivial exchange transformations. Braiding of MBS is at the core of current proposals regarding topological quantum computation.

The STM has become a major tool in the study of MBS and used to infer new properties on the states themselves. The fore-mentioned STM manipulation can be used to create atomically precise spin chains on superconductors. The new in-gap states evolve into bands and open gaps displaying new forms of superconductivity. This proves the complexity of the in-duced electronic structure. Each added impurity locally creates a few states in the superconducting gap. As the number of impurities grows, the gap fills up with new quasiparticle states.

The study of impurity dimers illustrates the initial steps of in-gap bands. The quasiparticle states themselves are difficult to describe. In the Bogolioubov-de Gennes approximation, the quasiparticle states are taken as electron and hole superpositions despite violating particle-number conservation. Furthermore, the quasiparticle states are spin polarized, which has important implications in the way the in-gap states hybridized. In particular, the resulting states reflect the spin-ordering of the magnetic impurities. However, recent work suggests that in the presence of strong Rashba coupling, it is difficult to conclude on the actual spin orientation of the impurities by studying the in-gap states.

Here, we study atomic spin chains of Cr adsorbed on the hollow sites of $\beta$-Bi$_2$Pd and grown along the two main surface directions, the $\langle 100 \rangle$ and $\langle 110 \rangle$ for the Bi-terminated [001] surface using a home-built dilution fridge STM. By doing so, we are choosing two starkly different spin orientations for the chain ground state as concluded in Ref. 32. Dimers along the $\langle 100 \rangle$-direction with a Cr-Cr distance of two unit cells (2$a$, where a is the surface lattice parameter) present antiferromagnetic (AFM) coupling of their $\frac{5}{2}$ magnetic moments. Dimers along the $\langle 110 \rangle$-direction are $\sqrt{2}a$ apart, and they are instead ferromagnetically (FM) coupled. Here, we compare dimers, trimers and tetramers of these two types of chains and conclude that the $\sqrt{2}a$--$\langle 110 \rangle$ chains are indeed FM coupled by comparing with model calculations of spin chains solving the Bogolioubov-de Gennes equa-
tions\textsuperscript{29,32}. As clearly seen in this work, the gap closes rapidly for the $\sqrt{2}a-(110)$ chains, however the $2a-(100)$ chains maintain an almost constant gap for chains as long as 12 Cr atoms. This has important implications for the possibility of engineering topological phases on the $\beta$-Bi$_2$Pd superconductor.

II. METHODS

A. Sample preparation and STM/STS characterization

The $\beta$-Bi$_2$Pd crystal was fabricated by the method written in Ref. 38. The chosen sample showed a $T_c$ of 5.2 K. The Bi-terminated surface of the $\beta$-Bi$_2$Pd crystal was prepared by exfoliation in-situ\textsuperscript{32}. Cr atoms were deposited onto a precooled $\beta$-Bi$_2$Pd surface at a temperature $T \leq 20$ K to have single isolated atoms. The experimental data were taken using a home-built dilution fridge STM at $T = 30$ mK and in ultra-high vacuum at the IBS Center for Quantum Nanoscience\textsuperscript{37}. The very-low temperature leads to a negligible thermal smearing granting a resolution higher than the one obtained by a superconducting tip\textsuperscript{39-41}. We used a metallic PtIr tip that permitted us to use the differential conductance, $dI/dV$, as a direct measurement of the density of states of the substrate (refer to the supplementary materials\textsuperscript{42} for more details). The conductance was measured using a lock-in amplifier with AC modulation bias 30 $\mu$V and frequency 330 Hz.

Lateral atomic manipulation was achieved by approaching the STM tip to one side of a selected atom to reach junction resistances in the order of a few tens of kΩ (typically 3 mV and tens of nA). Then the STM tip was laterally moved to drag the atom to a desired position with the feedback loop open.

B. Theory

We model the Cr spin chain in the dilute spin chain limit\textsuperscript{13} because density-functional-theory (DFT) calculations show that no Cr d-states lie at the Fermi energy, preventing charge transfer processes\textsuperscript{42}. In this framework, we solve a spin-chain using Green’s functions for the superconductor in the Nambu basis set\textsuperscript{43,44}. We add a Rashba term to the Hamiltonian expressed in the local basis. The resulting density of states corresponds to the Bogoliubov-de Gennes states of a BCS superconductor in the presence of an array of classical spins and subject to the strong Rashba interaction of the Bi-terminated surface.

The Fermi velocity entering the superconductor’s Green function\textsuperscript{43,44} is taken to be 0.15 (Hartree atomic units $\hbar = m = e = 1$) and the Dynes parameter\textsuperscript{45} controlling the width of the superconducting quasiparticle peaks is 0.05 meV. This leads to peaks in the density of states (DOS) sharper than the experimental ones, but helps the visualization of the evolution of in-gap states with the number of Cr atoms. $\beta$-Bi$_2$Pd is an s-wave superconductor that can be well accounted for by a single gap\textsuperscript{38,46} $\Delta = 0.76$ meV. For the normal metal DOS, we use $N = 0.037/eV$ that is 5 times larger than the corresponding $N$ for a free-electron metal with Fermi velocity of 0.15 atomic units, in order to capture the 5 electrons of the Bi valence shell. The Hamiltonian taking into account the superconductor is:

$$\hat{H}_{BCS} = \xi_k \tau_0 \sigma_3 + \Delta \tau_2 \sigma_2$$

Where $\sigma_i$ ($\tau_i$) are the Pauli matrices acting on the spin (particle) sectors. $\xi_k$ is the energy from the Fermi level ($\xi_k = \epsilon_k - E_F$), the previous Hamiltonian is written in the 4-dimensional Nambu basis: $\Psi = (\hat{c}_\uparrow, \hat{c}_\downarrow, \hat{c}_\uparrow^\dagger, \hat{c}_\downarrow^\dagger)^T$.

To model the experimental system, we add the Hamiltonian describing the magnetic impurities\textsuperscript{43,44}. To do this, we change to a tight-binding basis, assuming a single, very-compact, atomic orbital per site. Additionally, the interactions with the magnetic impurity is assumed to be strictly localized to the site where the impurity is sitting\textsuperscript{13}. The Hamiltonian is then:

$$\hat{H} = \hat{H}_{BCS} + \hat{H}_{impurity} = \hat{H}_{BCS} + \sum_j (U_j \tau_3 \sigma_0 + J_j \hat{S}_j \cdot \vec{\sigma})$$

with $\vec{\sigma} = \frac{1+\tau_3}{2} \vec{\sigma} + \frac{1-\tau_3}{2} \vec{\sigma}_3 \vec{\sigma}_2$, where $\vec{\sigma}$ is the spin operator\textsuperscript{9}. This Hamiltonian describes a BCS superconductor and the interaction between its electrons and $N$ extra impurities. The interaction contains an exchange coupling, with strength $J_j$, and a non-magnetic potential scattering term, $U_j$, per impurity $j$. We will use the same impurity species, Cr, and assume that they are equivalent regardless of their adsorption site and spin chain, in order to study the system’s evolution with the number of atoms in the spin chains. And $\hat{S}_j = (S_{j,x}, S_{j,y}, S_{j,z}) = S(\sin \theta_j \cos \phi_j, \sin \theta_j \sin \phi_j, \cos \theta_j)$ is the spin of atom $j$ considered to be a classical spin and hence not an operator. The local term $U_j$ describes a scalar potential acting on the substrate’s electron. It is responsible for the potential scattering term produced by the impurity. In the case of a charged impurity, $U_j$ is mainly given by the Coulomb interaction between the total charge of the impurity and the charge of the substrate’s electron. The potential scattering that explains the electron-hole asymmetry of the YSR bands is taken as $U_j = 5.5$ eV. The values for the Kondo-exchange coupling, $J_j$, are about 2 eV as estimated from fittings to a single-Cr YSR states\textsuperscript{32}.

The Hamiltonian is completed by a Rashba term:

$$\hat{H}_{Rashba} = i \frac{\alpha_R}{2a} \sum_{i,j,\alpha,\beta} [\hat{c}_{i+1,j,\alpha}^\dagger (\sigma_2)_{\alpha,\beta} \hat{c}_{i,j,\beta} - \hat{c}_{i,j+1,\alpha}^\dagger (\sigma_1)_{\alpha,\beta} \hat{c}_{i,j,\beta} + h.c.]$$

where $\alpha, \beta$ are spin indexes. The interaction couples spins on nearest-neighbour sites. The lattice parameter of the
substrate is $a$, and the factor of $2a$ comes from a finite-difference scheme to obtain the above discretized version of the Rashba interaction. For the case of Bi$_2$Pd, we use a large Rashba coupling, $\alpha_R \approx 1.8$ eVÅ as coming from our DFT calculations and in agreement with the couplings of Bi-terminated surfaces$^{47}$.

The local or projected DOS (PDOS) is computed over every local orbital $i$ of the basis using,

$$
\rho(i, \omega) = -\frac{1}{\pi} \text{Im}[G_{i,i}^{1,1}(\omega) + G_{i,i}^{4,4}(-\omega)]
$$

(4)

Where $G_{i,i}^{\nu,\mu}$ is the resulting Green’s function evaluated on orbital $i$ for the Nambu components $\nu$ and $\mu$ by solving Dyson’s equation:

$$
\hat{G} = [\hat{G}_{BCS}^{-1} - \hat{H}_I]^{-1}
$$

(5)

Where $\hat{G}_{BCS}$ is the retarded Green’s operator for the BCS Hamiltonian from Eq.(1) and $\hat{H}_I = \hat{H}_{impurity} + \hat{H}_{Rashba}$.

The DFT calculations were performed using the VASP code$^{48}$. The $\beta$-Bi$_2$Pd slab was optimized using the Perdew-Burke-Ernzerhof (PBE) form of the generalised gradient approximation (GGA)$^{49}$, following the calculations of Ref. 32. For more details, please see the supplementary materials$^{42}$.

III. RESULTS AND DISCUSSION

The $dI/dV$ over a single Cr adatom yields a single YSR state given by peaks at $V = \pm 0.35$ mV (please see Refs. 32 and 42). By lateral atomic manipulation, we place Cr atoms to create linear $\sqrt{2}a - (110)$ or $2a - (100)$ chains. Figure 1 (a) and (b) show constant-current images of the two tetramer chains. The (a) chain corresponds to the $\sqrt{2}a - (110)$ tetramer as depicted in the inset, the (b) is the $2a - (100)$ tetramer. As the chain is made larger, misplacing a Cr atom becomes more common. Indeed, error-free $\sqrt{2}a - (110)$ spaced nanostructures were difficult to obtain, while $2a - (100)$ chains are easier to manipulate. The reason lies in the chemistry of the chains. For the more compact chains, the affinity of Cr atoms for certain conformations leads to non-linear arrangements. The less compact $2a - (100)$ chain is easier to fabricate by single-atom manipulation because the atoms do not approach each other as much and hence cluster formation is much less common.

Our DFT calculations yield a coherent picture with the experiment. The Cr atoms are preferentially adsorbed on the hollow sites of the Bi-riched surface$^{32}$, and the Cr–Cr interactions in the chains are mediated by a single Bi atom in the $\sqrt{2}a - (110)$ chains or a square of four Bi atoms in the $2a - (100)$ chains. Short $1a - (100)$ chains can also be obtained, but the structures easily become clusters due to the Cr-Cr interaction. The $\sqrt{2}a - (110)$

FIG. 1. Chromium chains built on $\beta$-Bi$_2$Pd surface by atomic manipulation. Topographic images of (a) $\sqrt{2}a - (110)$ and (b) $2a - (100)$ unit-cell apart tetramer chains (100 mV, 10 pA, 4 × 4 nm$^2$). The insets show the atomic geometry of the tetramer nanostructures. The corresponding differential conductance is measured at the end atom (marked black dot) from dimer, trimer to tetramer in (c) $\sqrt{2}$ unit-cell apart and (d) 2 unit-cell apart tetramer chains. ($T = 30$ mK, AC modulation bias 30 $\mu$V)
FIG. 2. Differential conductance measured along Cr$_n$ $2\sqrt{2}a - \langle 100 \rangle$ chains with $n = 2$ in (a), $n = 3$ in (b), $n = 4$ in (c), $n = 6$ in (d), $n = 8$ in (e), $n = 9$ in (f), $n = 11$ in (g), $n = 12$ in (h). The $x$-axis represents the sample bias, the $y$-axis displays the distances over the chain. The color code gives the intensity of the differential conductance. The smallest gap in the system, defined as the distance between the lower quasiparticle peak and the highest quasihole peak is plotted in (i). In the absence of Cr atoms, the gap corresponds to $2\Delta$ where $\Delta = 0.75$ meV for Bi$_2$Pd. The gap has been obtained at an edge atom or at the center of the spin chain.

dimer is 249 meV less stable than the $1a - \langle 100 \rangle$ dimer. As a consequence, shifting a single Cr atom towards another Cr to reach the short $\sqrt{2}a$ distance likely produces a $1a - \langle 100 \rangle$ dimer. This stacking error becomes more likely as the chain is manipulated more times to make it longer. The $2a - \langle 100 \rangle$ dimer is only 30 meV less stable than the $\sqrt{2}a - \langle 110 \rangle$. But, still the interactions between atoms for the larger Cr–Cr distance, $2a - \langle 100 \rangle$ chains, are weaker resulting in an easier manipulation to build longer chains. Indeed, the bottom-up approach of chain building is difficult on many other substrates$^{50}$. Recent experiments show long Mn chains built in a similarly compact geometry as here but on a Nb(110) substrate, also giving rise to topological in-gap behavior$^{51,52}$.

Once the chains are built, the differential conductance, $dI/dV$, as a function of bias, $V$, and surface position, is an extraordinary probe of the electronic properties of the new systems. Figure 1 (c) and (d) shows $dI/dV$ spectra measured at $T = 30$ mK for the dimer, trimer and tetramer of $\sqrt{2}a - \langle 110 \rangle$ and $2a - \langle 100 \rangle$ type, respectively. The $dI/dV$ spectra are taken at an edge atom (black dot in Fig. 1 (a) and (b)). The two sets (c) and (d) are starkly in contrast. Figure 1 (c) clearly shows an in-gap state that is shifting towards zero bias as the chain gets longer. With opposite behavior, Fig. 1 (d) shows no clear in-gap state and a well-formed gap. Furthermore, the gap for the dimer is larger but the trimer and tetramer show similar gaps, pointing at a rapid stabilization of gap with chain size.

The in-gap states of the $\sqrt{2}a - \langle 110 \rangle$ dimer agree well with a model of two FM aligned spins and they disappear if the magnetic moments are coupled AFM as in Fig. 1 (d) for a $2a - \langle 100 \rangle$ dimer$^{32}$. The $2a - \langle 100 \rangle$-dimer behavior can be justified by the mutual cancellation of both spins, although the actual explanation is more involved. This can be seen by studying the spatial distribution of the differential conductance along the two types of chains. Figure 2 and 3 show the $dI/dV$ in a color code (bright-yellow corresponds to larger conductance and dark-blue represents zero conductance) along the chain, $y$-axis in Å of the distances over the chain, and $x$-axis in mV of the STM junction’s bias.

Figure 2 shows the results for the $2a - \{100\}$ spin chains. As seen in Fig. 1 (d), we find no obvious struc-
ture in the gap in any of the studied chains. A closer look reveals atomic modulations of the quasihole states that match the number of atoms in the chains. The presence of YSR states can be inferred by the profile of the gap.

The complete sequence of chains from $n = 2$ to $n = 12$ can be found in the supplemental material\cite{supplemental_material}. All chains roughly show a smaller gap at the edge atoms than at the center of the chain, see Fig. 2 (i). In first approximation, the gap is constant with chain length. Beyond 8 atoms, the chains show a smaller gap at the edge. However, the closing of the gap is very small and almost constant for longer chains. These data indicate that the YSR states are not able to close the superconducting gap, preventing any topological phase transition.

Figure 3 presents the $dI/dV$ maps of the $\sqrt{2}a - (110)$ chains (upper row) compared to model calculations of the PDOS on the surface sites (lower row). Figure 3 shows excellent agreement between experiment and theory if the magnetic moments are FM coupled, which is also in good agreement with the results of Ref. 32. The calculations of the YSR structure confirm the FM ordering for Cr atoms sitting along the $\sqrt{2}a - (110)$ hollow sites. Moreover, the magnetic ordering is not altered by adding extra atoms to the dimer.

The data of Fig. 3 permit us to have a clear picture of the in-gap states for the $\sqrt{2}a - (110)$ chains. The dimer presents two YSR bands, one closer to zero energy with a larger density of states between the two Cr adatoms, and one closer to the quasiparticle continuum with a minimum between the atoms. Adding one more atom to form the trimer shifts the lowest-energy YSR state closer to zero, but keeps its overall spatial distribution with a maximum PDOS on the central atom. Furthermore, we find the second band closer to the quasiparticle continuum, and again with a minimum of PDOS over the central point of the chain. We also notice that as in the dimer case, the quasiparticle PDOS presents a reduction and an oscillation along the chain. Finally, the tetramer shifts both bands closer to zero, but largely keeping their spatial distributions. The PDOS at the quasiparticle edge presents the same features as for the dimer and trimer.

In order to match the very fast experimental closing of the gap with the chain length, the Kondo exchange coupling ($J$) is increased from $J = 2.0$ eV for the dimer, $J = 2.1$ eV for the trimer, and $J = 2.3$ eV for the tetramer, respectively in Fig. 3 (d), (e) and (f). This behavior can be rationalized by a possible geometrical and electronic rearrangement of the chain as the spin chain grows in size. The atoms place themselves more symmetrically and closer to the surface leading to a larger hybridization with the substrate and thus to larger couplings.

The MBS appear naturally as soon as the exchange coupling $J$ is larger than 2.3 eV. It is interesting to study how the appearance of MBS takes place as $J$ varies. This is plotted in Fig. 4. The panels are arranged in three columns. Each column corresponds to a different value of $J$. The first one is $J = 2.1$ eV, the second one $J = 2.3$ eV and the fourth one is $J = 2.5$ eV. The first row plots the PDOS along the chain ($y$-axis) as a function of the quasiparticle energy ($x$-axis). We see the formation of YSR bands already for this 20-atom chain. In the middle of the chain, there is a clear gap in the YSR structure. For small $J$, this gap is maintained all along the chain, for the larger $J$, the gap is closed by an edge state that is a MBS as we shall briefly see. For $J = 2.3$ eV, we
see that the lowest-energy bands are still separated by a very small gap, almost closing and for \( J = 2.5 \) the gap is well-formed again. The closing and reopening of the gap is a necessary condition to change to a topologically non-trivial superconducting band structure.

The second row is the transversal spin density component \( \langle S_x \rangle \) along the chain for the same YSR state as above. We see that the values are small and dispersed for \( J = 2.1 \) and 2.3 eV. For \( J = 2.3 \) eV the values of \( \langle S_x \rangle \) extend all over the superconducting gap giving the impression of many YSR states closing the gap. But \( J = 2.5 \) eV is very different. The gap in \( \langle S_x \rangle \) is again clear and very sharp values at just the edge states appear and are of opposite sign. This is a clear signature of a MBS\(^5\).

The third row shows the spin of the YSR states. From the above data, we have evidence that a topological phase transition (TPT) has taken place between \( J = 2.1 \) eV and \( J = 2.5 \) eV, \( J = 2.3 \) eV being near to the closing of the gap. The spin shows it unambiguously. The YSR bands show opposite spin polarizations for their particle and hole components. This is clearly seen across the YSR gap. But the character has changed between \( J = 2.1 \) eV and \( J = 2.5 \) eV because the spin polarization is the opposite one. This is a clear hallmark of a TPT\(^5\). The edge states show the same spin polarization as corresponds to the MBS\(^5\).

The experimental data show that the gap is almost closed for the tetramer \( Cr_4 \sqrt{2}a - (110) \) spin chain. Closing the gap is a necessary condition for a topological phase transition (TPT). Figure 4 clearly show that the edge states for \( J \) larger than 2.3 eV are indeed MBS, and that the TPT takes place somewhere close to 2.3 eV. The change of YSR band character through the TPT is clearly seen in the YSR spin polarization\(^4\), indeed the spin inverts across the transition.

Figure 5 shows the calculation of a \( Cr_{20} \sqrt{2}a - (110) \) spin chain with \( J = 2.5 \) eV. A clear spin-polarized edge state appears, with opposite transversal spin components \( \langle S_x \rangle \) on the chain edges showing that indeed MBS are formed\(^3\). The number of atoms in the spin chain is decisive to clearly show MBS. However, short chains may suffice to prove that indeed the superconductor undergoes a TPT.

For a spin chain in the topological phase, the appear-
The behavior of MBS with the chain’s length is shown in Fig. 6 for $Cr_n \sqrt{2}a - \langle 110 \rangle$ chains with $n$ from 5 to 20. The parameters are the above ones with $J = 2.5$ eV that correspond to the topological phase. In the case of the pentamer, Fig. 6 (a) clearly shows a closed gap. We find a zero-energy state for $Cr_5$ that looks very similar to the experimental (and theoretical) one for $Cr_4$. The zero-energy state is clearly localized in the center of the chain. As the chain length is increased, the state localizes to the edges. At the same time there is an excitation gap appearing in the center of the chain. For $n = 8$ atoms, it is already possible to clearly differentiate the features of the well-formed MBS even though the chain is still small and the YSR states present a strong discrete nature. As the length is increased, a clear MBS appears. These calculations imply that $Cr_n \sqrt{2}a - \langle 110 \rangle$ chains on $\beta$-Bi$_2$Pd will clearly show MBS and topological features at fairly small chains. Indeed, 20 atoms suffice to have an unambiguous topological spin chain.

IV. CONCLUSION

In summary, $Cr_n \sqrt{2}a - \langle 110 \rangle$ spin chains on $\beta$-Bi$_2$Pd show a fast closing of the superconducting gap as the number of atoms in the chain increases. As few as four Cr atoms suffice to have in-gap states closing down the gap. We show that an 8-atom $\sqrt{2}a - \langle 110 \rangle$ chain may already display all features of MBS. Our study reveals that the $\sqrt{2}a - \langle 110 \rangle$ Cr spin chain shows ferromagnetic alignment of its spins. The large magnetic moment of Cr plus a sizable Rashba coupling of the $\beta$-Bi$_2$Pd surface leads to the topological phase transition. Increasing the distance between Cr atoms leads to facile atom manipulation that translates in longer chains of Cr atoms on $\beta$-Bi$_2$Pd but at the cost of not reaching a topological phase. Indeed, our measurements show a persistent gap rather constant with chain length for $Cr_n 2a - \langle 100 \rangle$, showing that this type of chains will not induce a topological phase transition on the $\beta$-Bi$_2$Pd superconductor.
FIG. 6. $Cr_n \sqrt{2}a -(110)$ chains with $n$ from 5 to 20, for $J = 2.5$ eV such that the superconductor is in the topological phase. The zero-energy state moves away from the center of the chain to the borders as the chain is increased in size. At fairly low numbers, 8 or even 7 atoms, the MBS become clear and a gap is formed at the center of the chain.

ACKNOWLEDGEMENT

Financial support from the Spanish MICINN (projects RTI2018-097895-B-C44 and Excelencia EUR2020-112116), Euskal Jaurlaritza (project PIBA_2020_1_0017), JSPS KAKENHI (JP18K03531 and JP19K14651), and the Institute for Basic Science (grant IBS-R027-D1) is gratefully acknowledged.

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Supplementary Material for: Atomic Manipulation of In-gap States on the $\beta$-Bi$_2$Pd Superconductor

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(Dated: May 7, 2021)

COMPARISON OF THE Dl/dV SPECTRA USING METALLIC AND SUPERCONDUCTING TIPS

We used a dilution fridge STM operating at $T = 30$ mK [1]. The benefit of measuring at a very-low temperature leads to a negligible thermal smearing granting a higher energy resolution in a range of a few tens of $\mu$eV. Measuring with a superconducting tip increases the energy resolution due to the sharp quasi-particle peaks at the tip side [2] but afterward, a deconvolution process is required to get the density of states of the sample [3, 4]. Figure 1 shows the comparison of the dI/dV spectra measured using a superconducting tip at 1.2 K and a non-superconducting metallic tip at 30 mK. We use a metallic PtIr tip that permitted us to use the $dI/dV$ as a direct measurement of the density of states of the substrate without any deconvolution process.

LOCAL SPECTRA OF THE CR$_n$, 2a – (100) SPIN CHAINS

Figure 2 shows all the spectra obtained along the spin chains formed by Cr$_n$, 2a – (100) on $\beta$-Bi$_2$Pd with $n = 2, \cdots, 12$. The evolution is very smooth and the features are very similar. Namely, the in-gap states are very close to the superconductor’s quasiparticle peaks, and a clear, almost constant gap is maintained. Beyond $n = 8$, the gap measured at the edge slightly closes down, and an excited-state edge state starts developing. However, as far as $n = 12$ the gap at the edge stays constant and there is no indication of any gap closing for Cr$_n$, 2a – (100) on Bi$_2$Pd. The gap has been evaluated by taking the distance between peaks in the second derivative, $d^2I/dV^2$, after a 5-point smoothing of the experimental data.

DENSITY FUNCTIONAL THEORY CALCULATIONS

The DFT calculations were performed using the VASP code [5]. The calculations performed here extend the ones in Ref. [6]. The $\beta$-Bi$_2$Pd slab was optimized using the Perdew-Burke-Ernzerhof (PBE) form of the generalised gradient approximation (GGA) [7], obtaining a bulk lattice parameter $a = b = 3.406$ Å and $c = 13.011$ Å in good agreement with other DFT calculations and the experimental value of $3.36(8)$ Å and $12.97(2)$ Å given in Ref. [8]. The surface calculations were performed for Bi-terminated slabs with four Bi layers and two Pd ones. The surface unit cell was taken as a $6 \times 4$ lattice, where two Cr atoms can be placed at 2a without interaction between dimers. The k-point sampling was $1 \times 3 \times 1$. The structures were relaxed until forces were smaller than 0.01 eV/Å for the three topmost layers and the Cr structures.

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FIG. 1. Comparison of the differential conductance measured on a single Cr atom (blue curve) and on a bare β-Bi$_2$Pd surface (black curve) with superconducting and non-superconducting tips. The $dI/dV$ spectra using (a) a superconducting (coated with Bi$_2$Pd) tip at $T = 1.2$ K (adapted from Ref. 6) and (b) a normal metallic PtIr tip at $T = 30$ mK.

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FIG. 2. Differential conductance measured along for \( \text{Cr}_n \) \( 2a - \langle 100 \rangle \) chains with \( n = 2 \cdots 12 \). Figure 2 of the main text reproduces some of the panels of this figure. The gap has been obtained at an edge atom or at the center of the spin chain. In both cases the gaps are constant within the experimental error.