Probing magnetic interactions between Cr adatoms on the
$\beta$-Bi$_2$Pd superconductor

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Abstract

We show that the magnetic ordering of coupled atomic dimers on a superconductor is revealed by their intra-gap spectral features. Chromium atoms on the superconductor $\beta$-Bi$_2$Pd surface display Yu-Shiba-Rusinov bound states, detected as pairs of intra-gap excitations in the tunneling spectra. We formed Cr dimers by atomic manipulation and found that their intra-gap features appear either shifted or split with respect to single atoms. The spectral variations reveal that the magnetic coupling of the dimer changes between ferromagnetic and antiferromagnetic depending on its disposition on the surface, in good agreement with density functional theory simulations. These results prove that superconducting intra-gap state spectroscopy is an accurate tool to detect the magnetic ordering of atomic scale structures.
Magnetic impurities have a detrimental effect on superconductivity [1]. The exchange interaction between the atomic magnetic moments and Cooper pairs produces localized bound states inside the superconducting (SC) gap, known as Yu-Shiba-Rusinov [2–4] states (Shiba states in the following). Previous scanning tunneling spectroscopy measurements found that Shiba states can be detected in magnetic adatoms on a superconducting surface [5] as very sharp intra-gap peaks in their quasiparticle excitation spectra [6, 7]. The position of the peaks inside the gap is very sensitive to the exchange interaction of the impurity with the surface [8], whereas their number can be related to the amount of spin-polarized atomic orbitals [9, 10] and the spin’s multiplet in the presence of anisotropy [11].

In spite of the local character of the atomic scattering potential, the amplitude of Shiba wavefunctions can extend over several nanometers [9, 12] and interfere with other Shiba states of close-by impurities [6, 13]. It has been predicted that the sub-gap spectral features of a pair of interacting impurities depend on the alignment of their magnetic moments [14]. Hybridization of Shiba states in atomic-scale structures is a prerequisite for the formation of extended Shiba-bands [15], which under certain circumstances may develop exotic properties such as topological superconductivity [16, 17]. Therefore, examining the character of Shiba-hybridization at the atomic scale and its relation with the magnetic alignment of the impurities is crucial.

Here we study quasiparticle excitation spectra of Cr atomic dimers on the surface of the superconductor $\beta$-Bi$_2$Pd and show that they reveal the alignment of their magnetic moments. We use the tip of a scanning tunneling microscope (STM) to manipulate individual Cr atoms and form atomically precise dimers with different interatomic orientations and distances. Differential conductance measurements on the Cr dimers reveal that their Shiba states shift or split with respect to those on isolated atoms depending on the dimer’s arrangement on the surface. Furthermore, the spatial distribution of the hybridized Shiba states resemble either anti-bonding or bonding components of a "Shiba molecule" [14, 18–20]. With the support of density functional theory (DFT) simulations, we conclude that the evolution of Shiba states in each case is originated by either the antiparallel or parallel alignment of the dimer’s atomic magnetic moments.

Our experiments were carried out on the Bi-terminated surface of a $\beta$-Bi$_2$Pd crystal (see Methods in Supplementary Information (SI) [23]), cleaved under ultra-high-vacuum (UHV) conditions, and subsequently transferred in situ into a cryogenic STM for measurements at
FIG. 1: Cr atoms on the Bi-terminated $\beta$-Bi$_2$Pd surface. (a) Atomic resolution of a Bi-terminated clean $\beta$-Bi$_2$Pd surface in a constant height mode with the junction resistance of $15k\Omega$ (size: $3 \times 3$ nm$^2$). (b) STM image of Cr atoms deposited on the Bi-terminated $\beta$-Bi$_2$Pd surface ($V = 1$ V, $I = 10$ pA, size: $10 \times 10$ nm$^2$). (c) Results of a full DFT relaxation showing that the most stable position of a Cr atom (green) is at hollow site (Bi atoms in pink and Pd atoms in bronze). Differential-conductance spectra measured (d) on the bare surface and (e) on a Cr adatom, using a superconducting $\beta$-Bi$_2$Pd tip. Tunneling between coherent peaks of tip and sample results in sharp dI/dV peaks at $\pm 2\Delta/e$ (dashed lines in the plots). (f) Density of states obtained by deconvoluting the tip DOS from the spectra on the Cr adatom (blue) and on the bare surface (black). Analysis of STM and STS data was performed with the WSxM [21] and SpectraFox [22] software packages.

T=1.2 K. The exposed surface is atomically clean and shows a squared atomic structure (Fig. 1a), with periodicity in agreement with the $\beta$-Bi$_2$Pd unit cell (lattice parameter $a = 3.36$ Å). Next, we evaporated small amounts of Cr atoms on the pristine surface at low temperature ($T = 15$ K) to obtain Cr densities similar to that shown in the STM image of Fig. 1b. Individual Cr adatoms appear as protrusions 110 pm high, absorbed on hollow sites of the bismuth surface. This agrees with the minimum energy configuration obtained from Density Functional Theory (DFT) simulations, shown in Fig. 1c and in the SI [23].

The stoichiometric compound $\beta$-Bi$_2$Pd is a s-wave superconductor with a single gap of magnitude $\Delta = 0.76$ meV [24]. The superconducting properties are very isotropic [25], leading to a narrow gap distribution of just a few tens of $\mu$eV wide [24], in spite of its square Fermi surface [26, 27]. We determined the LDOS of pristine and Cr-decorated regions by means of differential conductance (dI/dV) spectra. To enhance the spectral resolution,
FIG. 2: (a)–(d) STM image of Cr dimers at indicated spacings (V=1 V and I=10 pA, size:3×3 nm²). The square mesh depicts the surface β-Bi₂Pd lattice. (e)–(h) Differential conductance spectra on the atom indicated by a white dot before (gray) and after (red) the second atom is moved to the dimer position. As in Fig. 1, all spectra are measured using superconducting tips with the same ∆ as the substrate (dashed lines mark the ±2Δ/e bias). The corresponding tip-deconvoluted DOS is shown in the lower panels.

we employed superconducting STM tips obtained by indenting a W tip into the β-Bi₂Pd surface, which has an isotropic single superconducting gap. As a consequence, the tunneling spectra result from the convolution of tip and sample LDOS [6, 8, 28]. The dI/dV spectrum of the pristine β-Bi₂Pd surface, Fig. 1d, shows a conductance gap with two sharp peaks at ±1.52 mV, i.e. at ±2Δ/e, due to tunneling between quasiparticle (QP) peaks at ±Δ in tip and sample. Typical dI/dV spectra acquired on top of single Cr adatoms (Fig. 1e) show smaller QP-peaks and a pair of additional peaks inside the spectral gap (at V=±1.1±0.1 mV) indicating the formation of Shiba states at the locations of the adsorbed Cr atoms. Figure 1f compares the LDOS of pristine surface and Cr adatoms extracted from the tunneling spectra following the deconvolution procedure of Refs. [10, 29].

To explore the effect of magnetic interactions on Cr Shiba states, we studied the evolution of intra-gap spectral features of Cr atomic dimers constructed by STM lateral manipulation. Figs. 2a–d show STM images of the four types of dimers that show sizable spectral variations. The atoms are separated by (a) d = √5a, (b) d = 2a, (c) d = 1a and (d) d = √2a,
corresponding to distances between hollow sites. For larger Cr-Cr separations, the dI/dV spectra are unaffected by the neighboring adatom. In every case, we measured the dI/dV spectrum of a target Cr adatom first isolated (grey in Figs. 2e–h), and then after a second adatom is precisely positioned nearby (red in Figs. 2e–h). The spectrum on the \( d = \sqrt{5}a \) dimer shows only a faint effect of the interaction between atoms (Fig. 2e). When their separation is reduced to \( d = 2a \), the Shiba peaks appear closer to the SC gap edge \( (\epsilon \sim 450 \mu eV, \text{Fig. 2f}) \), overlapping with the QP peaks of the superconductor and evolving into broader spectral features. Finally, at very short distances \( (d = 1a) \), the Shiba excitations are absent from the spectrum, which now show symmetric but broader QP peaks (Fig. 2g). The observed tendency is that Shiba peaks shift towards the QP continuum as the interatomic distance decreases.

Interestingly, when the Cr adatoms are moved to contiguous hollow sites along the surface diagonal, \( d = \sqrt{2}a \), the spectra show a more complex structure with additional features close to the QP peaks (Fig. 2h). In this case, the DOS is composed of two intra-gap peaks for particle states and two peaks for hole states with separation of \( \sim 250 \pm 50 \mu eV \). This pattern resembles the splitting of hybridized Shiba states predicted for atoms interacting ferromagnetically \([14, 18–20]\).

To interpret the observed evolution of intra-gap spectra in terms of the magnetic alignment of the Cr spins, we show in Fig. 3 the simulated DOS of a ferromagnetic (FM) \( \sqrt{2}a \) dimer, and the corresponding dI/dV spectrum, obtained using an extension of Flatté and Reynolds model \([14]\) (details in SI \([23]\)). The model parametrizes first the electron-Cr interaction of a Cr monomer on the \( \beta\)-Bi\(_2\)Pd substrate to fit their experimental spectral features. Using this parametrization, the model reproduces a splitting of Shiba states for the \( \sqrt{2}a \) dimer if the two spins of the Cr atoms are assumed to be parallel. Imposing an antiferromagnetic (AFM) alignment to the magnetic moments of a \( 2a \) dimer leads instead to a single Shiba peak (Fig. 3a), as observed in the experiments. The model further captures the additional role of potential scattering in the subgap states, which induces a small asymmetry in particle and hole energy of the states for both AFM and FM cases. These results thus confirm that interacting Shiba states of Cr atoms can evolve into molecular-like states with bonding and antibonding configurations depending on the type of magnetic order.

The different type of Shiba hybridization is reflected in their respective spatial distribution of bound-state excitation amplitude \([14]\). Figure 4a and 4c show the spectral maps (i.e.}
FIG. 3: Model calculation of the Shiba density of states (DOS) of (a) an antiferromagnetically ordered dimer separated by $d=2a$ and (b) a ferromagnetically ordered one at $d=\sqrt{2}a$ (see [23]). For both dimer structure, ferromagnetic order leads to split Shiba peaks, while AFM shows only a degenerate one. Panels (c) and (d) shows the corresponding dI/dV spectra obtained by convoluting the dimer’s DOS with a superconducting tip DOS.

dI/dV vs distance and bias) measured along the axis of the $2a$ and $\sqrt{2}a$ dimers, respectively. In all cases, the amplitude of the QP peaks decreases substantially over the dimer and a distinct pattern of sub-gap excitations emerges for every atomic arrangement. For the $2a$ dimer, the amplitude of the Shiba peaks is clearly maximum over each atom and shows a nodal plane in between, both for particle and hole components (Fig. 4b). This is in good agreement with predictions for the AFM case [14], picturing the hybridized Shiba states as degenerate states localized around each of the two impurities. In contrast, the $\sqrt{2}a$ dimer shows a different pattern for each of the split Shiba states. The state with lower energy appears with more amplitude in the region between the two atoms, while the higher one shows a nodal plane between them (see Fig.4c). This is clearly visualized in dI/dV spatial maps at each excitation energy (Fig. 4d), showing a bonding and anti-bonding pattern for the lower and higher Shiba states, respectively.

Density function theory further confirms the magnetic ordering of the adsorbed dimers. We first calculated the adsorption properties of a single Cr atom on $\beta$-Bi$_2$Pd. The calculations find that Cr adatoms preferentially adsorb on the hollow site, with a subsurface Pd
FIG. 4: Topography profiles and spectral (dI/dV vs. V) maps measured along the axes of the (a) 2a and (c) $\sqrt{2}a$ dimers (gray-scale covers dI/dV range from 0 to 0.3 $\mu$S). Top panels in (b) and (d) correspond to the dimer STM image, scanned at 3 meV and 10 pA. Below, we show the 2D spatial distribution of the differential conductance at the bias of the Shiba peaks for (b) the 2a dimer (size: $3 \times 3$ nm$^2$) and (d) the $\sqrt{2}a$ dimer (size: $2.5 \times 2.5$ nm$^2$), at the given energies.

atom directly underneath, as shown in Fig. 1c. As a result of the bonding interaction, the adatom’s next-neighbor Pd and Bi atoms slightly approach towards the Cr adatom by 10 pm and 5 pm, respectively inducing a small distortion of the surface (see SOM). The Cr adatom lies 1.59 Å above the surface layer and keeps a total magnetic moment of 4.4 $\mu_B$, close to the 5 $\mu_B$ of a free atom. The large spin polarization of the system can be pictured by isosurfaces of the electronic density difference between majority and minority spins, shown in Fig. 5a. The Cr atom polarizes the four nearest-neighbour Bi atoms antiferromagnetically, and the second-layer Pd atoms ferromagnetically.

Next, we calculated the adsorption properties of the different types of dimers found in the experiment. The most stable dimer configuration on the surface has both atoms absorbed on contiguous hollow sites separated by a distance d=1a. This corresponds to the compact dimer shown in Fig. 2c and Fig. 5b. The two atoms interact strongly and approach, reducing the Cr-Cr distance by 80 pm (from $a=3.46$ Å to d=2.74 Å). The Cr atoms are clearly antiferromagnetically coupled with an energy 152 meV lower than the ferromagnetic configuration ($E_{AFM}-E_{FM}=\Delta E=-152$ meV). The 2a dimer shows a much weaker interatomic interaction, and each Cr appears with a negligible deviation from the single adatom adsorption geometry. Their atomic spins interact indirectly via the substrate with a slight preference for antiferromagnetic ordering ($\Delta E=-10$ meV), in agreement with
FIG. 5: Spin polarization (a) of a Cr adatom and of various dimers (d=1a (b), 2a (c) √2a (d)) on the β-Bi$_2$Pd surface. In each case, the results correspond to the minimum-energy configuration obtained from DFT simulations of the relaxed system. The plot shows 3D isosurfaces of constant electronic density difference between majority and minority spins, in the normal state. The surface is tilted differently in every case to picture the extension of the spin density to inner layers. Bi atoms are represented in pink and Pd atoms in bronze. The isocontours of spin are yellow and red for each of the two spin components (the isocontour is 0.005 e/Å$^3$ in all graphs).

The assignment from the experiments. The spin density of the 2a configuration (Fig. 5c) pictures this antiferromagnetic arrangement in the ground state. It also shows that the intermediate Bi atoms have a stronger magnetic polarization, suggesting that these atoms might mediate the interaction between Cr adatoms.

The dimer along neighbouring diagonal sites (d= √2a in Fig. 2d and Fig. 5d) shows a clear preference for a ferromagnetic ground-state, with ∆E=19 meV, again in good agreement with the interpretation of Shiba spectral features. Interestingly, both Cr atoms appear connected via a single Bi atom (Fig. 5d), which shows opposite magnetization and, probably, forces the ferromagnetic ordering of the dimer.

The DFT results thus confirm the magnetic ordering deduced from the analysis of Shiba
states. Both \(1a\) and \(2a\) dimers are antiferromagnetically aligned, in agreement with the measurement of a single pair of intra-gap excitations. The observed shift of the Shiba excitations towards the gap edge with reducing Cr–Cr distance reflects the weakening of the bound state’s energy, probably due to the reduction of the total magnetization of antiferromagnetically coupled dimers. For the \(\sqrt{2}a\) dimer, the splitting of Shiba states and their peculiar bonding-antibonding spatial distribution reflect the ferromagnetic coupling of the dimer.

In summary, we demonstrated that the spectral features of coupled Shiba states reflect the magnetic ordering of interacting atoms. We proved this by studying dimers of Cr atoms on a superconducting \(\beta\)-Bi\(_2\)Pd surface, assembled by atomic manipulation using a low-temperature STM. Differential conductance spectra reveal sub-gap excitations associated to Shiba states, which evolve as the atoms are brought to proximity, reflecting their mutual spin alignment. We found that different atomic arrangements on the surface result in shifts or splits of the atomic Shiba features. Furthermore, the spatial distribution of the Shiba peaks for the \(\sqrt{2}a\) dimer resembles bonding and antibonding states, as predicted for a ferromagnetic dimer. DFT simulations confirm the magnetic ordering deduced from the spectra analysis. Therefore, the measurement of Shiba excitation spectra of magnetically coupled impurities is an excellent probe of their magnetic ordering.

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See Supplemental Material, for a description of the model Hamiltonian calculations of the coupled Shiba states, the DFT results, as well as additional experimental data.

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Note 1 - Sample preparation and the spectra of vacancies and defects on $\beta$-Bi$_2$Pd surfaces

The experiments were performed on $\beta$-Bi$_2$Pd crystals grown from high-purity Bi (Alfa Aesar 99.99%) and Pd (Alfa Aesar 99.95%) following the procedure described in Ref. [1]. STM/STS measurements were carried out in an UHV low-temperature Joule-Thomson STM at a base temperature of 1.15 K. The differential conductance was measured using lock-in detection with a modulation of 40$\mu$V rms at 938.6 Hz. Analysis of STM and STS data was performed with the WsXm [2] and SpectraFox [3] (http://www.spectrafox.com) software packages.

To increase the energy resolution beyond the limit imposed by the Fermi-Dirac distribution of a metallic tip, we use in our experiments superconducting tips prepared by gently dipping a W-tip into the $\beta$-Bi$_2$Pd surface. This process was repeated until sharp d$I$/d$V$ peaks due to tunneling between coherent peaks of tip and sample appeared separated by a $4\Delta/e$ bias gap ($\Delta=0.75$ meV is the order parameter of $\beta$-Bi$_2$Pd) in the tunneling spectra of the bare $\beta$-Bi$_2$Pd surface. Although a superconducting tip with the bulk order parameter was easily obtained, the energy resolution achieved by these tips varies depending on the experiment.

In Fig. 1(a) we show an STM image of the pristine $\beta$-Bi$_2$Pd surface. Atomic-scale protrusions and vacancies (seeing as depressions) were frequently observed over a $50 \times 50$ nm$^2$ scanned area. As shown in Fig. 1(b), on both types we measure identical tunneling spectra as on the bare surface regions. From this, we conclude that there is no magnetism associated with the adatoms or the vacancies. This contrast with the spectra on deposited Cr atoms, which shows a very characteristic fingerprint, as we show in the main text. Since our samples are cleaved in ultra-high vacuum conditions, the protrusion cannot be related to contaminants. Instead, it is probable the protrusions are Bi adatoms extracted from the observed vacancies on the Bi surface layer during cleaving.

![STM image and tunneling spectra](image)

FIG. 1: Bare surface of the $\beta$-Bi$_2$Pd surface after the in-situ exfoliation. (a) Topographic image over $50 \times 50$ nm$^2$ (scanned at 100mV, 10pA). (b) The differential conductance measured on the defect and the vacancy compared with the one on the bare surface.
Note 2 - Hamiltonian model for Yu-Shiba-Rusinov states of a chain of atoms

The Shiba-chain state and conductance simulation were performed solving the BCS Hamiltonian in real space in the presence of $\delta$-like exchange, $J_i$, and scattering, $K_i$, potentials following Refs. [4, 5]. The model Hamiltonian can then be written as:

$$\hat{H} = \hat{H}_{BCS}^0 + \sum_{i=1}^{N_{at}} (J_i \vec{S}_i \cdot \vec{\alpha} + K_i \tau_3) \delta(\vec{r} - \vec{r}_i).$$

Here $N_{at}$ is the number of atoms of the Shiba chain and $i$ is the index for each atom of the chain. The Pauli matrices for the spin ($\vec{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$) and electron-hole ($\vec{\tau} = (\tau_1, \tau_2, \tau_3)$) sectors are explicitly considered in $\vec{\alpha}$ as [6]:

$$\vec{\alpha} = \frac{\vec{1}_\tau + \tau_3}{2} \otimes \vec{\sigma} + \frac{\vec{1}_\tau - \tau_3}{2} \otimes \sigma_2 \vec{\sigma}$$

corresponding to the Nambu spinor [6]:

$$\Psi(\vec{r}) = \begin{pmatrix} \psi^*_\uparrow(\vec{r}) \\ \psi^*_\downarrow(\vec{r}) \\ \psi_\uparrow(\vec{r}) \\ \psi_\downarrow(\vec{r}) \end{pmatrix}$$

To represent the $\beta$-Bi$_2$Pd superconductor we used for simplicity a single-band BCS Hamiltonian $\hat{H}_{BCS}^0$ with the largest Fermi velocity ($v_F = 0.4 \times 10^6$ m/s), and with gap $\Delta = 0.76$ meV, as determined in Ref. [1] and [7].

The resolvent or Green’s function of the BCS Hamiltonian can be written as a function of the distance $r$ of two points, $r = |\vec{r} - \vec{r}'|$, in the translationally-invariant superconductor as [5]:

$$G_{BCS}^0(\vec{r}, \vec{r}', \omega) = -\frac{\pi N_0}{k_F} e^{-\frac{\sqrt{\Delta^2 - \omega^2}}{\xi}} r \times$$

$$\begin{pmatrix} \frac{\omega}{\sqrt{\Delta^2 - \omega^2}} \text{sink}_{F \tau} + \text{cosk}_{F \tau} & 0 & 0 & -\frac{\Delta}{\sqrt{\Delta^2 - \omega^2}} \text{sink}_{F \tau} \\ 0 & \frac{\omega}{\sqrt{\Delta^2 - \omega^2}} \text{sink}_{F \tau} - \text{cosk}_{F \tau} & \frac{\Delta}{\sqrt{\Delta^2 - \omega^2}} \text{sink}_{F \tau} & 0 \\ 0 & \frac{\Delta}{\sqrt{\Delta^2 - \omega^2}} \text{sink}_{F \tau} & \frac{\omega}{\sqrt{\Delta^2 - \omega^2}} \text{sink}_{F \tau} + \text{cosk}_{F \tau} & 0 \\ -\frac{\Delta}{\sqrt{\Delta^2 - \omega^2}} \text{sink}_{F \tau} & 0 & 0 & \frac{\omega}{\sqrt{\Delta^2 - \omega^2}} \text{sink}_{F \tau} - \text{cosk}_{F \tau} \end{pmatrix}$$

here, $\xi = h v_F / \pi \Delta$ is the coherence length, $k_F$ the Fermi wave-vector, and $N_0$ the normal metal density at the Fermi energy. Following the careful study by Vernier [8], we see that the limit $r \to 0$ is:

$$G_{BCS}^0(\vec{r}, \vec{r}, \omega) = -\pi N_0 \text{Sign}[Re(\omega)Im(\omega)] \begin{pmatrix} \frac{\omega}{\sqrt{\Delta^2 - \omega^2}} & 0 & 0 & -\Delta \\ 0 & \frac{\omega}{\sqrt{\Delta^2 - \omega^2}} & \Delta & 0 \\ 0 & \Delta & \frac{\omega}{\sqrt{\Delta^2 - \omega^2}} & 0 \\ -\Delta & 0 & 0 & \frac{\omega}{\sqrt{\Delta^2 - \omega^2}} \end{pmatrix}$$

3
The non-collinear Shiba chain problem can be treated now with a Dyson equation where the self-energy is local thanks to the \( \delta \)-interaction and given in Nambu-spinor form by:

\[
\Sigma_{i,i} = \begin{pmatrix}
J_i S_i \cos \theta_i + K_i & J_i S_i \sin \theta_i e^{-i\phi_i} & 0 & 0 \\
J_i S_i \sin \theta_i e^{i\phi_i} & -J_i S_i \cos \theta_i + K_i & 0 & 0 \\
0 & 0 & -J_i S_i \cos \theta_i - K_i & -J_i S_i \sin \theta_i e^{i\phi_i} \\
0 & 0 & -J_i S_i \sin \theta_i e^{-i\phi_i} & J_i S_i \cos \theta_i - K_i
\end{pmatrix}
\]

(5)

where each spin \( \vec{S}_i \) is now given by its modulus \( S_i \) and two angles \( \theta_i \) and \( \phi_i \). The Dyson equation can now be solved in the tight-binding basis of each atom, \( \psi_i(\vec{r}) \) and STM data can be simulated by the local density of states:

\[
\rho(\vec{r},\omega) = -\frac{1}{\pi} \text{Im} \{ tr \sum_{i,j} \psi_i(\vec{r}) \hat{G}_{i,j}(\omega) \psi_j^*(\vec{r}) \frac{\hat{\tau}_3 + \hat{1}}{2} \}.
\]

(6)

**Note 3 - Simulation of Yu-Shiba-Rusinov states and sub gap spectra of Cr dimers**

We have approximated the conductance over dimers of Cr atoms on a \( \beta \)-Bi\(_2\)Pd superconductor using a BCS superconductor and two localized magnetic moments (of 5 Bohr magnetons each, according to our DFT simulations in Note 4) at different distances. We employed the model described in Note 2, which ignores any direct exchange interaction between Cr atoms. Thus, only the BCS superconductor reacts to the presence of the magnetic moments by the appearance of in-gap bound states. These Shiba states can interact through the BCS superconductor, giving rise to bonding/antibonding states if the two Cr spins are aligned parallel or to a single bound state for the antiferromagnetic alignment.

We evaluate the local density of states to approximate the STM data. The calculations are first performed for a single Cr atom. We find that the experimental spectra (position and amplitude of Shiba excitations) are best fitted for a exchange coupling \( J \) of 1.8 eV and a scattering potential \( K \) of 5.5 eV. In order to compare with the experiment, we further convolute the data by the tip’s and sample’s BCS DOS. This leads to the appearance of the QP coherent peak that is otherwise absent of the DOS on the Cr atoms. From a typical spectrum on the bare substrate we fit an effective Dynes damping of 20 \( \mu \)eV and a tip gap of \( \Delta \approx 700 \mu \)eV. In the simulations we also added Gaussian broadening of 70 \( \mu \)eV to take into account different sources of noise (AC voltage from the lock-in amplifier and superconducting gap distribution). With these parameters we reproduce the dI/dV spectrum of a single Cr atom.

Next, we evaluate the full set of data for the dimers without any extra parameters, only the distance between Cr atoms and the relative orientation of the atomic magnetic moments characterize the dimers. Figure 2a and 2b show the DOS and dI/dV spectrum for the \( \sqrt{2}a \) dimer, respectively. The plots show both the simulations imposing parallel (FM) and antiparallel (AFM) Cr magnetic moments. We see that the splitting observed in the experiments is retrieved for the FM case. Figure 2c and 2d shows similar results for the \( 2a \) dimer. Note that in this model there are no atomistic details. Therefore, the \( 2a \) dimer simply corresponds to a dimer with larger interatomic distance. In this case, the single pair of Shiba excitations is observed for the AFM alignment, instead.
Note 4 - DFT simulations

To better understand and interpret our experimental findings, we performed DFT calculations on this system. The calculations were performed using the VASP code [9]. The $\beta$-Bi$_2$Pd slab was optimized using the Perdew-Burke-Ernzerhof (PBE) form of the generalised gradient approximation (GGA) [10], obtaining a bulk lattice parameter $a = b = 3.406$ Å and $c = 13.011$ Å in good agreement with other DFT calculations [11] and the experimental value of 3.36(8) Å and 12.97(2) Å given in Ref. [1]. 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. The magnetic configurations were evaluated by fixing the collinear atomic magnetic moments, breaking spin symmetry.

First we calculated the stability of a single Cr atoms adsorbed on different positions of the $\beta$-Bi$_2$Pd surface. The calculations show that Cr adatoms preferentially adsorb on the hollow site where one Pd atom is directly underneath. As a result of the interaction, the Pd atom shifts by 0.1 Å towards the Cr away from the Pd layer. The hollow site is preferred
with an adsorption energy of -2.00 eV per Cr atom, vs -1.45 eV of the bridge site and -1.13 eV of the top site. The total magnetic moment of the Cr atom goes from 5 \( \mu_B \) in the gas phase to 4.4 \( \mu_B \) on the hollow site, 4.75 \( \mu_B \) on bridge and 4.96 \( \mu_B \) on top, showing the demagnetisation of the atom as it gets more strongly bound to the surface. The Cr adatom lies 1.59 Å above the Bi surface layer producing a small expansion of the local Bi-Bi distance to 3.45 Å from the computed Bi-Bi distance of 3.405 Å.

Experimentally, the built structures can be classified by the Cr-Cr distance in units of the lattice parameter \( a \) (see main text). We calculated the adsorption properties for different types of dimers by placing atoms in proximal hollow sites, and their respective stability is described in the main text.

We also calculated the absorption of a compact dimer formed by two Cr atoms on a hollow site, with a Cr-Cr distance of 1.58 Å, equal to the free-dimer one. In this case, the antiferromagnetic order of the free dimer persist on the surface, resulting in an unpolarized singlet state with negligible magnetic interaction with the surface. The adsorption energy is 95 meV less favorable than for the antiferromagnetic 1\( a \) dimer. So we discard that these structures appear on the surface.

Figure 3 (a) shows the density of states projected on the electronic structure of an isolated Cr atom. The strong magnetization of the Cr atom is preserved upon adsorption as seen by the clear separation of both spins components of the projected DOS. A slight charge transfer and a sizeable broadening of the atomic levels reveal a non-negligible interaction with the surface in agreement with the above values for the atomic adsorption energy and demagnetization. Figure 3 (b) shows the density of states projected on the Cr \( d \)-manifold of one of the Cr atoms of the 2\( a \) dimer. The resemblance with the previous case is notable, showing that the 2\( a \) dimer in a zero order approximation can be considered as independent Cr atoms. However a certain deformation of the PDOS can be seen close to the Fermi energy, implying a small degree of electronic hybridisation between the two atoms. This hybridisation is slightly larger for the 1\( a \) dimer, Fig. 3 (c), albeit still very small. Overall, the local environment of the hollow site controls the main features of the PDOS on the eV scale and thus, the PDOS is largely equivalent for the three previous cases.

As a comparison, we show in Figure 3 (d) the PDOS on compact Cr\(_2\) dimer adsorbed on a hollow site (black lines). The PDOS has no resemblance with the single Cr one. Indeed, the magnetic moment is much reduced leading to less difference between majority and minority spin. The same figure shows the PDOS on one of the two Cr atoms of the gas-phase dimer (red lines), for comparison. We retrieve the same features as for the adsorbed Cr\(_2\) compact dimer, except that in the latter case the interaction with the surface leads to a substantial broadening of the electronic states.

Calculations revealing the spin polarization and ground state magnetic ordering of the systems are shown in the main text. Adsorption of Cr along the troughs of the bismuth top-most layer of \( \beta \)-Bi\(_2\)Pd leads to antiferromagnetic spin ordering. Along the diagonal of the surface, the \( \sqrt{2}a \) and the \( 2\sqrt{2}a \) dimers show ferromagnetic ordering. However, the energy difference to an antiferromagnetic alignment is small (19 and 6 meV respectively), and further studies are needed to conclude on the actual DFT values.

Despite of the large spin-orbit coupling of the Bi layer, our calculations with explicit spin-orbit coupling show that the antiferromagnetic ordering is favored at short distances along the surface troughs. However, calculations with larger unit cells should be performed to be able to conclude on more complex non-collinear patterns.
FIG. 3: Density of states projected (PDOS) on a Cr for (a) a single Cr atom adsorbed on the hollow site of the β-Bi$_2$Pd surface, (b) on one of the Cr atoms of a 2-unit cell apart, 2a, dimer, the Cr atom is adsorbed on a hollow site, (c) on one of the Cr atoms of a 1a dimer, and (d) on one of the Cr atoms of a dimer adsorbed along the surface diagonal centered on the hollow site (black) compared with the free-dimer PDOS (red). Full lines are the PDOS on the majority spin and dashed lines on the minority spin.

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