Projective Quasiparticle Interference of a Single Scatterer
to Analyze the Electronic Band Structure of ZrSiS

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Abstract

Quasiparticle interference (QPI) of electronic states has been widely applied in scanning tunneling microscopy (STM) to analyze electronic band structure of materials. Single-defect-induced QPI reveals defect-dependent interaction between a single atomic defect and electronic states, which deserves special attention. Due to weak signal of single-defect-induced QPI, the signal-to-noise ratio (SNR) is relatively low in a standard two-dimensional QPI measurement. In this paper, we develop a projective quasiparticle interference (PQPI) method, in which a one-dimensional measurement is taken along high-symmetry directions centered on a specified defect. We apply the PQPI method to a topological nodal-line semimetal ZrSiS. Two types of atomic defects are found to scatter the surface and bulk electronic bands. With enhanced SNR in PQPI, the energy dispersions are clearly resolved along high symmetry directions. An orbital-selective scattering is confirmed and explained by different overlaps between tip and sample wavefunctions. Furthermore, an energy shift of the surface floating band is observed and a new branch of energy dispersion ($q_0$) is resolved. This PQPI method can be applied to other complex materials to explore defect-dependent interactions in the future.
I. INTRODUCTION

In scanning tunneling microscopy (STM), quasiparticle interference (QPI) of electronic states has been a powerful tool to analyze the electronic band structure of condensed matter materials [1–21]. QPI arises when the electronic state with initial momentum \( k_i \) is elastically scattered to a final momentum \( k_f \). The potential barrier of scattering is often induced by point defects, steps or other local perturbations in materials. The scattering process leads to a spatial oscillation of electronic state with wave vector \( q = k_f - k_i \). The wave vector can be extracted from Fourier transform of QPI oscillations. As a function of energy \( E \), the \( q(E) \) dispersion reflects the electronic band structure in \( k \)-space.

The QPI study initially focused on electronic surface state, whose QPI oscillation (or Friedel oscillation) decays slowly with increasing distance from the scattering center [1–4]. QPI has been thereafter applied in both surface states of materials, and electronic structure of two-dimensional (2D) materials [5–8]. On the other hand, parallel features in Fermi surface structure may cause anisotropic propagation of a three-dimensional (3D) band, which can also result in a strong QPI oscillation on sample surface [9]. The development of QPI technique enables extensive analysis of band structure of complex materials, including high-\( T_c \) superconductors [10–12], heavy fermion systems [13, 14], and topological materials [15–21].

Although all QPI oscillations are related with the underlying electronic band structure, QPI induced by a single scatterer deserves special attention [19, 20, 22, 23]. Different types of point defects trigger defect-dependent interaction between the defect and electronic states. The QPI analysis around specified point defects can reveal selection rules in the scattering process. For example, in topological nodal-line materials ZrSiS and ZrSiSe [24, 26], two different types of point defects are found to scatter electronic states of the floating surface band [30, 34] and bulk band, respectively [27, 30]. In ZrSiSe, a single scatterer to scatter both the surface and bulk bands was observed [29, 30], which hasn’t been detected yet in ZrSiS.

However, the QPI signal around a single scatterer is relatively weak, resulting in a low signal-to-noise ratio (SNR) in Fourier-transformed QPI pattern. The vague band structure in this analysis limits data-based discussions of physical properties. Here in this paper, two new types of point defects are discovered in ZrSiS, and a projective QPI (PQPI) method
is developed to analyze the scattered electronic bands, with a much higher SNR. The first new type defect scatters both surface and bulk band, while the second new type defect only scatters the bulk band. With the PQPI method, we could clearly resolve an orbital-selective scattering within the bulk band, and explain it with different overlaps between tip and sample wavefunctions. Furthermore, we also observe a possible defect-induced energy shift of the floating surface band, and an extra bulk band dispersion of $q_6$ branch. PQPI is a simple and intuitive method which can be applied in general single scatterer induced QPI studies of different materials.

II. EXPERIMENTAL METHOD

Single crystals of ZrSiS were grown by a two-step chemical vapor transport method using iodine as transport agent [31]. In the first step, a stoichiometric amount of 99.9 % purity precursors of Zr:Si:S = 1:1:1 molar ratio was pressed into tablet, and put in an alumina crucible. After sealed in an evacuated quartz ampoule, the sample was treated at 1100 °C for two days and then furnace-cooled to room temperature. In the second step, the tablet of ZrSiS was ground into fine powder and then sealed in an evacuated quartz ampoule with 5mg/cm3 iodine. The quartz ampoule was treated in a two-zone tube furnace with a thermal gradient of about 1100 °C - 950 °C. After a period of 8 days, single crystals of ZrSiS were obtained.

STM measurements were carried out in a commercial ultra-high vacuum system [29, 32]. The samples were cleaved in situ at liquid nitrogen temperature and immediately inserted into the STM head. An electrochemically etched tungsten tip was treated with field emission on a single crystalline of Au(111) surface. A bias voltage $V_b$ was applied to the sample, and the tunneling current collected from the tip was maintained at a fixed setpoint $I_s$ by a feedback loop control. All data were acquired at liquid helium temperature (≈ 4.5 K).

III. RESULTS AND DISCUSSION

The family of ZrSiX (X = S, Se, Te) shares a layered crystal structure. In Fig. 1(a), The crystal structure of ZrSiS shows a square lattice of Si atoms is sandwiched between two sets of ZrS bilayers with glide mirror symmetry [24, 33]. For STM experiment, the single crystal
sample was cleaved between two ZrS bilayers, with a S layer naturally exposed to be the surface plane. Figure 1(b) displays a typical topography taken on the exposed S surface, with a tunneling junction of $V_b = 600$ mV and $I_s = 1$ nA. In the topography, a clear square lattice can be observed with interatomic spacing of $a_0 \approx 3.6$ Å. For the family of ZrSiX, the density of states (DOS) around Fermi level is mainly contributed by $d$ electrons of Zr atoms [24]. Top sites of the square lattice are determined to be at locations of Zr atoms, even though Zr atoms are structurally below the surface plane of S atoms.

Different from that in ZrSiSe [29], our ZrSiS experiment shows a bias-independent topography, without a shift of square lattice for different bias-voltage polarities. In a clean area of the sample, the measured $dI/dV$ spectra are separately averaged over the top, hollow and bridge sites. As shown in Fig. 1(c), the averaged spectra are almost indistinguishable. They all exhibit a nonzero and V-shaped DOS around the Fermi level (zero bias), while the DOS of occupied state is smaller than that of the empty state. The spatially homogeneous spectrum is consistent with the bias-independent topography.

In Fig. 1(b), sparse point defects of different types can be observed within the square lattice. A typical diamond- and X-shaped defects are enlarged in the top row in Fig. 1(d), whose centers are at Zr and S sites, respectively. In previous STM studies of both ZrSiS and ZrSiSe [27–30], the diamond (X-shaped) defects are found to selectively scatter the electronic surface band (bulk band). For ZrSiSe, a strong scatterer is found to scatter both the surface and bulk bands [29], which is hitherto not reported in ZrSrS. In the bottom row of Fig. 1(d), we show two new types of atomic point defects in ZrSiS, QPI around which are the main focus of this paper.

The bottom left defect in Fig. 1(d) is centered at the Zr site, around which a larger topography ($16 \times 16$ nm$^2$) is shown in Fig. 2(a). To study QPI around a single atomic defect, a standard method is to obtain the differential conductance ($dI/dV$) maps from spectroscopy measurement. For a single $dI/dV$ map, a quick procedure is to collect the $dI/dV$ signal at the fixed bias voltage while scanning the tip in constance current mode. Along with the constant-current topography in Fig. 2(a), a $dI/dV$ map was taken simultaneously at $V_b = 300$ mV. As shown in Fig. 2(b), this $dI/dV$ map exhibits an obvious pattern of standing wave centered around the point defect, referred as a QPI image later. The standing wave originates from the point-defect-induced scattering between electronic states of different wave vectors (initial $k_i$ and final $k_f$) but the same energy. In Fig. 2(b), the QPI image is
not azimuthally symmetric, but shows strong oscillations along the lattice direction and the diagonal (45°) direction. Fourier transform of the $dI/dV$ map is calculated and drawn in Fig. 2(c). Similar to previous reports for ZrSiSe [29], the Fourier-transformed QPI pattern can be mainly partitioned into three groups: the central diamond, the outer concentric square, and four sets of parallel lines around Bragg peaks.

The QPI pattern is described in the momentum $q$ space with $q = k_f - k_i$. Figure 2(d) shows a contour of constant energy (CCE) model similar as that in Ref. 29. For the floating surface band [30 34], there are four pairs of short parallel arcs around four X points. The scattering between parallel arcs in the same pair ($q_1$) corresponds to the central diamond in the QPI pattern. Scattering between short arcs in diagonal pairs ($q_2$) corresponds to the parallel lines around Bragg peaks in the QPI pattern. For the bulk band, two concentric squares in the CCE model may contribute to concentric squares in the QPI pattern, with possible wave vectors $q_3$, $q_4$ and $q_5$. In the QPI pattern in Fig. 2(c), the scattering of both the surface band and bulk band can be identified, confirming the discovery of a new type of scatter in ZrSiS. For the concentric squares in the QPI pattern, either a single square or two squares have been found for different point defects in ZrSiX [27–30]. Without a high SNR in the QPI pattern, it is hard to judge whether the results are intrinsic characteristics of the point defect or just vague and indistinct signals with limited SNR.

To study the energy dependent QPI pattern, a three-dimensional (3D) dataset has to be taken. For each spatial point in the scan area, the feedback loop is temporarily interrupted and a $dI/dV$ spectrum is taken in a selected voltage range, with the energy $E = eV$. After the measurement, the energy-dependent $dI/dV$ maps can be extracted from the 3D dataset for further analysis. A long time measurement is necessary in this process (e.g. 12-24 hours), in which the system instability and thermal-drift affect the SNR. To display the energy-dependent QPI results, Fourier-transformed results are often shown along high symmetry directions in $q$ space and plotted as a function of the energy. As shown in Fig. 2(f), the Fourier-transformed result is displayed along high symmetry direction, from $(1, -1)\pi/a_0$ to $(-1, 1)\pi/a_0$ in $q$-space (red line in Fig. 2(c)). The concentric square in the QPI pattern intersects with this line at the wave vector $q$, later confirmed as $q_3$. The energy dependent dispersion of $q_3$ is correspondingly labeled in Fig. 2(f). Similarly, Figure 2(g) shows the Fourier-transformed result along the orange line in Fig. 2(c), from one Bragg peak of $(1, 0)2\pi/a_0$ to the diagonal Bragg peak of $(-1, 0)2\pi/a_0$ in $q$-space. The diamond
in the QPI pattern intersects with this line at \( q_1 \), and the dispersion of \( q_1 \) is labeled in Fig. 2(g). We can observe a limited SNR in the energy dependent results, which hinders a precise extraction of dispersions of \( q_3 \) and \( q_1 \) branches.

Here in this work, we develop a simple and intuitive method, a projective quasiparticle interference (PQPI) on single defect, to study the same energy dependent scattering and extraction of electronic band structure. In the two-dimensional QPI image (Fig. 2(a), the standing wave propagates strongly along the lattice direction and the diagonal direction. In this PQPI method, the \( dI/dV \) spectra were measured at dense spatial points along two corresponding linecuts as labeled in Fig. 2(a). With the decrease of dimension from 2D to 1D in the real space measurement, we could increase the average number in the spectroscopy measurement. The effect of system instability and thermal-drift is also lessened within the short measurement time (e.g. 0.5 hour for a single linecut).

In Fig. 3(a), the measured \( dI/dV \) spectrum is shown as a function of energy (each vertical line), along the linecut of diagonal direction. For each energy, the oscillating standing wave can be observed along the linecut in the real space. The real-space signal can be further Fourier-transformed, leading to the \( q \)-space QPI pattern along the high symmetry direction from \((1, -1)\pi/a_0\) to \((-1, 1)\pi/a_0\). As shown in Fig. 3(b), the \( q_3 \) branch is more clearly identified, from the strongly enhanced SNR in the PQPI measurement. In the meantime, there is no clear dispersion signal of scatter wave vector \( q_4 \) shown as red dash line in Fig. 3(b). Because of the short measurement time in PQPI, the energy range is enlarged to \([-400, 1000]\) meV with an energy resolution of 4 meV. A similar spectroscopy measurement was taken along the lattice direction, with the real-space data shown in Fig. 3(c). The Fourier-transformed results in \( q \)-space is shown in Fig. 3(d), in which the labeled \( q_1 \) branch exhibits a clearly resolved dispersion. With the relative high SNR, another \( q_6 \) branch is also identified, which will be discussed later. Putting Fig. 3(b) and 3(d) together, we can confirm that this special impurity scatters both electronic surface and bulk band, similar as the special defect found in ZrSiSe \[29\]. Only one \( q_3 \) branch is identified for the scattering within concentric squares.

Now we turn to the second type of special point defect. As shown in the bottom right image in Fig. 1(d), this type of defect is centered at the S site. A larger topography around this impurity was taken (Fig. 4(a)). For the same field of view, the \( dI/dV \) map at the bias voltage 300 mV was also simultaneously taken. As shown in Fig. 4(b), the standing wave
around this defect is observed to mainly propagate along the 45° direction with respect to the lattice direction. With one neighboring X-shaped defect, the QPI image of our interest is partially affected by the X-shaped-defect-induced standing wave. The \(dI/dV\) map in Fig. 4(b) is Fourier transformed, leading to the QPI pattern in \(q\) space in Fig. 4(c). The concentric squares appear in the center of the QPI pattern, while the diamond and four sets of parallel lines around Bragg peaks are absent. This defect seems only scatter the bulk band similar as the X-shaped defect. From the 3D spectroscopy dataset, figure 4(d) shows the extracted Fourier-transformed result along the \(q\)-space red line in Fig. 4(c), as a function of energy. We could roughly distinguish two dispersed lines, labeled as \(q_3\) and \(q_4\) branches, respectively.

For the PQPI measurement, two real-space lines are chosen in Fig. 4(a) to be away from the extra standing wave from X-shaped defect. The \(dI/dV\) spectrum was measured along the line of diagonal direction, whose Fourier transform is performed and shown in Fig. 4(e). Within a large range of energy, two dispersed branches (\(q_3\) and \(q_4\)) can be clearly identified, confirming the two vague dispersions in Fig. 4(e). Similarly, a series of \(dI/dV\) spectrums were measured along the line of lattice direction, whose Fourier-transformed results are presented in Fig. 4(g). Different from QPI pattern in Fig. 3, the \(q_1\) branch of dispersion is obviously absent, consistent with that in Fig. 4(c) and 4(f). The high SNR result in Fig. 4(g) confirms that this defect does not scatter the electronic surface band.

With the PQPI method, electronic branches from scattering can be clearly identified for different defects, which enables a precise extraction of dispersions and a quantitative analysis of the electronic band structure. For comparison, the electronic band structure of ZrSiS was also calculated with a density functional theory (DFT) of a slab model. The DFT calculations were carried out using the Vienna ab initio simulation package (VASP) [35–38]. An \(1 \times 1 \times 5\) supercell with a vacuum layer larger than 2 nm was applied in the slab model. Figure 5(a) shows the calculated band structure along the \(M-\Gamma-M\) direction in \(k\)-space. The orbital projection has been considered in the band calculation, as presented with different colored dots in Fig. 5(a).

From the DFT results, the bands near the Fermi surface are mainly contributed by different orbital components of Zr atoms. The outer band above the Fermi level with orange dots is mainly composed of \(d_{x^2-y^2}\) components, meanwhile the inner branch with red dots is composed of degenerated \(d_{xz}\) and \(d_{yz}\) components. The QPI branch with wave vector \(q_3\)
corresponds to the scattering between two internal bands originating from $d_{xz}$ & $d_{yz}$ orbitals of Zr atoms, or two sides of the internal square in the CCE model. The $q_1$ branch corresponds to the scattering between one band with $d_{xz}$ & $d_{yz}$ orbitals and another band with $d_{x^2−y^2}$ orbitals of Zr atoms. In the CCE model, it is equivalent to the scattering from one side of the internal square to the opposite side of the the outer square.

For the defect #1, we extract $q(E)$ from the dispersed line with high intensity in Fig. 3(b). In Fig. 5(d), the extracted $q(E)$ is well consistent with the $q_3(E)$ calculated from the electronic band structure, which proves that the single branch in Fig. 3(b) matches with $q_3$, instead of $q_1$ or $q_5$. For the defect #2, we extract two dispersed branches in Fig. 4(e). In Fig. 5(e), the two extracted branches are well consistent with $q_3(E)$ and $q_4(E)$ calculated from the electronic band structure. With the decreasing energy, the amplitudes of $q_3(E)$ and $q_4(E)$ increase, but at different speeds. The dispersion of $q_3(E)$ and $q_4(E)$ merge around the energy of 300 meV above the Fermi level, related with the nodal line in this nodal-line semimetal. The determination of nodal line is consistent with the result for ZrSiSe in the previous work [29].

For these two defects, we discover either a single branch of scattering with wave vector $q_3$ or two branches of scattering with wave vectors $q_3$ and $q_4$. This phenomenon is similar to that in previous literatures for ZrSiS and ZrSiSe [27, 28, 39]. The scattering of $q_5$ is never discovered heretofore. The high SNR in our results prove that the absence of scattering of $q_5$ is not due to a limited SNR in the QPI measurement, but an intrinsic property of the scattering. A possible mechanism to explain this phenomenon is to consider the orbital-selective scattering in QPI. The scattering of $q_3(E)$ branch happens between bands with $d_{xz}$ & $d_{yz}$ orbitals, and the scattering of $q_4(E)$ branch happens between bands with $d_{x^2−y^2}$ and $d_{xz}$ & $d_{yz}$ orbitals. In STM experiment, the tunneling current depends on the overlap between the tip and sample wavefunctions [40]. With a vertical $z$-component, $d_{xz}$ & $d_{yz}$ orbitals of Zr atoms are prone to be overlapped with the typical s-wave symmetric tip state [41]. The overlap between $d_{x^2−y^2}$ orbital (in the $xy$ plane) and the tip state is comparably smaller. The order in which the three branches are prone to be detected is $q_3$, $q_4$, and $q_5$, which explains why either $q_3$ branch or $q_3$ and $q_4$ branches are discovered in QPI patterns of ZrSiX materials.

We next discuss the scattering between electronic states in the surface band. Figure 3(b) shows the calculated band structure along the M-X-M direction, perpendicular to the two
parallel arcs in the CCE model in \(k\)-space. This surface band is called a floating band, originating from the surface-induced symmetry breaking from nonsymmorphic group \(P4/nmm\) to symmorphic wallpaper group \(P4mm\). With the broken symmetry, the high band degeneracies are not protected any more and can be lifted, resulting floating or unpinned two-dimensional surface band \(33\). In Fig. 5(f), we extract \(q_1(E)\) from the dispersed line with high intensity in Fig. 3(d). The main dispersion of \(q_1\) branch is linear from 300 meV up to 1 V. However, the calculated surface band has to be shifted 150 meV up to match the experimental results, despite a deviation at high energy level. This energy shift may show the sensitivity of the floating band position with respect to the impurity \(12\) \(13\).

In Fig. 3(d), with the high SNR in our PQPI method, a new branch of \(q_6(E)\) can be observed, which has never been reported in previous STM experiments. The branch of \(q_6(E)\) is extracted and shown in Fig. 5(g). After careful comparison, this branch is found to be consistent with the scattering between bulk bands along \(\Gamma X \Gamma\) direction (Fig. 5(c)). This bulk band has been identified in previous ARPES experiment \(26\), and further confirmed in a recent ARPES experiment using high energy photons \(44\).

IV. SUMMARY

PQPI is a complementary tool to analyze the single-defect-induced QPI pattern and its energy dependence. With a single defect as the scattering center, the QPI oscillation decays with increasing distance away from the defect. A standard \(dI/dV\) mapping of the QPI image is a 2D measurement within a small area around the defect. Although a long time is required in the data-taking procedure, SNR of the 2D measurement is still relatively low. With an anisotropic propagation of the scattering oscillations, some high symmetry directions can be chosen in the PQPI method, along which a 1D \(dI/dV\) measurement can be finished within a short time. Changing from a 2D measurement to an 1D measurement, we can increase the data-taking time of each single spectrum and enhance the SNR of measured results.

In summary, we investigate single-defect-induced QPI oscillations in the nodal-line semimetal ZrSiS. Two new types of defects are found to scatter the bulk bands and surface floating bands. With the application of PQPI method, clear QPI dispersions along high symmetry directions can be clearly resolved. We explain the orbital-selective scattering by different overlaps between tip and sample wavefunctions. An energy shift of the surface
floating band is observed and a new branch of \( q_6 \) is discovered. The PQPI method can be generally applied in other complex materials to explore the distinct interaction between a single atomic defect and electronic states.

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FIG. 1. (a) Crystal structure of ZrSiS, with a cleavage plane between S layers. Top view of the cleaved surface is shown on right. The yellow, green and blue dots represent S, Zr and Si atoms, respectively. (b) A 25 × 25 nm$^2$ topography of ZrSiS taking under $I_s = 1$ nA and $V_b = 600$ mV. The two perpendicular white arrows represent lattice directions. (c) The average $dI/dV$ spectra at the top (red), bridge (orange) and hollow (black) sites under $V_b = 500$ mV. Inset shows a supercell image of a 12 × 12 nm$^2$ clean area. (d) Four different point defects in topography under same bias voltage $V_b = 500$ mV.
FIG. 2. (a) A $16 \times 16$ nm$^2$ topography under $V_b = 300$ mV with defect #1 at the center. The orange and red line across the defect are along the lattice and diagonal directions, respectively. (b) The $dI/dV(V = 300$ mV) map simultaneously taken with (a). (c) Fourier transform of the $dI/dV$ map in $q$-space. (d) A CCE model in $k$-space, and (e) the calculated $q$-space map following this CCE model. (f-g) QPI energy dispersions along red and orange lines shown in (c).
FIG. 3. (a) Linecut measurement of $dI/dV$ spectrums along the red line in Fig. 2(a) for defect #1. (b) Fourier transform of the linecut measurement in (a). Maximum of energy dispersion is highlighted with a red solid line ($q_3$). A red dash line represents the absence of possible scattering of $q_4$ branch. (c) Linecut measurement of $dI/dV$ spectrums along the orange line in Fig. 2(a) for defect #1. (d) Fourier transform of the linecut measurement in (c). Maximum of two energy dispersions are highlighted with orange ($q_1$) and white ($q_6$) lines, respectively.
FIG. 4. (a) A 16 × 16 nm² topography under $V_b = 600$ mV with defect #2 at the center. (b) The $dI/dV(V = 300$ mV) map simultaneously taken with (a). (c) Fourier transform of $dI/dV$ map in $q$-space. (d-e) The energy dispersions along the M-Γ-M direction. The result in (d) is extracted from a standard 2D $dI/dV$ map along the red line in (c). The result in (e) is extracted from a linecut measurement along the red line in (a). Two red lines highlight the scattering of $q_3$ and $q_4$ branches. (f-g) The energy dispersions along the X-Γ-X direction. The results are extracted from two different datasets similar as described in (d-e). An orange dash line represents the absence of possible scattering of $q_1$ branch.
FIG. 5. (a-c) DFT calculation of the slab band structure along the M-Γ-M, M-X-M and Γ-X-Γ directions in $k$-space. The blue, green, red and orange dots represent $d_{xy}$, $d_{z^2}$, $d_{xz}$ & $d_{yz}$ and $d_{x^2-y^2}$ orbitals of Zr atoms respectively (d-e) Comparison of energy dispersions between experimental results and DFT calculations along M-Γ-M direction. (f-g) Comparison of two energy dispersions between experimental results and DFT calculations along X-Γ-X direction for defect #1. The surface band has to be shifted 150mV up to match with experimental results in (f).