Electronic structure of the titanium-based oxypnictide superconductor Ba\(_{0.95}\)Na\(_{0.05}\)Ti\(_2\)Sb\(_2\)O and direct observation of its charge density wave order


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Electronic structure of the titanium-based oxypnictide superconductor \( \text{Ba}_{0.95}\text{Na}_{0.05}\text{Ti}_2\text{Sb}_2\text{O} \) and direct observation of its charge density wave order


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\( \text{Ba}_{0.95}\text{Na}_{0.05}\text{Ti}_2\text{Sb}_2\text{O} \) is a titanium-based oxypnictide superconductor with possible density wave order. We have performed high resolution angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM) studies on \( \text{Ba}_{0.95}\text{Na}_{0.05}\text{Ti}_2\text{Sb}_2\text{O} \). Our STM studies find a charge density wave (CDW) order with the wavevector of \((\pi, \pi)\). The electronic structure shows both multi-orbital and three-dimensional nature, consistent with the theoretical calculations. The observed Fermi surfaces are well nested along the \((\pi, \pi)\) direction, which might drive the CDW transition. Likely due to the weak strength of the CDW order, we do not observe a leading-edge gap. Instead, we observe an overall spectral weight enhancement with decreasing temperature, but the rate of this enhancement is abruptly reduced or diminished in the CDW state, suggesting the suppression of spectral weight or opening of a partial CDW gap. Our results give a comprehensive picture of the electronic structure and direct observation of the CDW order in \( \text{Ba}_{0.95}\text{Na}_{0.05}\text{Ti}_2\text{Sb}_2\text{O} \).

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I. INTRODUCTION

Layered transition-metal compounds have proven a fruitful stage for novel superconductivity. Intriguingly in these systems, unconventional superconductivity usually emerges in proximity to a spin-ordered or charge-ordered state, for example, in cuprates, iron-based superconductors and layered chalcogenides [1–3]. This offers a clue about searching for unconventional superconductivity in layered compounds. The titanium pnictide oxides, such as \( \text{Na}_2\text{Ti}_2\text{P}_2\text{O}_7 \) and \( \text{BaTi}_2\text{P}_2\text{O}_7 \) (\( \text{Pn} = \text{As, Sb} \)), are layered systems with distinct transport anomalies that are associated with the formation of density wave order. The transition temperatures are 330 K for \( \text{Na}_2\text{Ti}_2\text{As}_2\text{O} \), 200 K for \( \text{BaTi}_2\text{As}_2\text{O} \), 115 K for \( \text{Na}_2\text{Ti}_2\text{Sb}_2\text{O} \) and 45 K for \( \text{BaTi}_2\text{Sb}_2\text{O} \), respectively[4–6]. So far, the exact nature of the density wave is still unknown, although no sign of spin density wave (SDW) have been found, there is also no direct evidence for a charge density wave (CDW) ground state. Nevertheless, they have been proposed as a candidate parent phase for superconductivity. Many attempts to induce superconductivity in both \( \text{Na}_2\text{Ti}_2\text{P}_2\text{O}_7 \) and \( \text{BaTi}_2\text{As}_2\text{O} \) by chemical substitution or Li intercalation have failed, although the temperature of CDW/SDW transition has been successfully suppressed[5].

Superconductivity emerges at 1 K in \( \text{BaTi}_2\text{Sb}_2\text{O} \) [7], and a maximal \( T_c \) of 5.5 K has been achieved in \( \text{Ba}_{1-x}\text{Na}_x\text{Ti}_2\text{Sb}_2\text{O} \) [8]. These make them the only known titanium-pnictide-oxide superconductors. First principles calculations of \( \text{BaTi}_2\text{Sb}_2\text{O} \) suggest that the density wave transition is caused by a magnetic instability associated with Fermi surface nesting, and the superconductivity is mediated by spin fluctuations [9]. However, another calculation indicates that a CDW instability may dominate, with the superconductivity driven by conventional electron-phonon interactions in this compound [10]. Experimentally, muon spin rotation (\( \mu \text{SR} \)) studies have not found any sign of magnetic order, while a nuclear magnetic resonance (NMR) observed broken in-plane four-fold symmetry at the Sb site without the presence of an internal field [11, 12]. Therefore, CDW order is more likely although no direct evi-
around the BZ boundary, $\overline{X}$. The low-lying states are contributed by Ti $d_{\overline{2}-\overline{2}}$, $d_{\overline{1}}$, and $d_{\overline{3}}$ orbitals. The Fermi surface is well nested along the $(\pi, \pi)$ direction. Although we do not observe a leading-edge gap in the density wave state, we find an overall spectral weight enhancement with decreasing temperature, and the rate of this enhancement is abruptly reduced or diminished below the density wave transition temperature. Furthermore, our STM studies have directly observed a CDW order with wavevector of $(\pi, \pi)$, consistent with the nesting wavevector observed by ARPES. Of particular note, our results indicate that the CDW strength in Ba$_{1-x}$Na$_x$Ti$_2$Sb$_2$O is weaker than in BaTi$_2$As$_2$O or Na$_2$Ti$_2$Sb$_2$O, which may be the reason for the emergence of superconductivity here.

II. EXPERIMENTAL

High quality Ba$_{0.95}$Na$_{0.05}$Ti$_2$Sb$_2$O single crystals were grown by a BaSb self-flux method. Ba pieces and Sb powder were mixed together, heated to 800 °C, and kept for 10 hours. Optimally doped polycrystalline Ba$_{0.75}$Na$_{0.25}$Ti$_2$Sb$_2$O polycrystals was synthesized with a superconducting transition temperature at 5.5 K from magnetic susceptibility measurements, following the growth recipe in Ref. 8. The powder was then mixed with BaSb flux in a ratio of 1:3. The mixture was loaded into an alumina crucible and then sealed in an iron crucible under Ar environment. It was preheated to 800 °C for 10 hours, then heated to 1350 °C for 5 hours, and finally slowly cooled to 1000 °C at a rate of 3 °C / hour before shutting off the power. Shiny single crystals could be found inside of the containing material. The composition of the single crystals was Ba$_{0.95}$Na$_{0.05}$Ti$_2$Sb$_2$O based on x-ray diffraction (XRD) measurements, different from the starting polycrystalline material.

The crystal structure of Ba$_{0.95}$Na$_{0.05}$Ti$_2$Sb$_2$O is shown in Fig. 1(a). The Ti, Sb, and O atoms formed Ti$_2$Sb$_2$O octahedron are stacked alternatively with layers of Ba/Na atoms along the c axis. Figures 1(b) and 1(c) show the magnetic susceptibility and resistivity data of Ba$_{0.95}$Na$_{0.05}$Ti$_2$Sb$_2$O, both of which exhibit an anomaly at 48.5 K, indicating a density wave transition. The heat capacity of the Ba$_{0.95}$Na$_{0.05}$Ti$_2$Sb$_2$O single crystal in Fig. 1(d) shows a superconducting transition around 1 K.

ARPES experiments were performed at the SIS beamline of Swiss Light Source (SLS, beamline 5-4 of Stanford Synchrotron Radiation Lightsource (SSRL) and beamline I05-ARPEPS of Diamond light source (DLS), all equipped with a Scienta R4000 electron analyzer. The angular resolution was 0.3° and the overall energy resolution was about 7 meV at the SLS, 10 meV at the DLS and above 10 meV at the SLS depending on different photon energies. The samples were cleaved in-situ along the (001) plane and measured under ultra-high vacuum below $9 \times 10^{-11}$ torr.

STM measurements were performed in a cryogenic STM system at 4.5 K. Platinum tips were used after treatment on Au surface. Topographic images were taken with constant current mode with the bias voltage applied to the sample. The tunneling conductance ($dI/dV$) was collected by standard lock-in
method with a modulation frequency of 973 Hz. The typical modulation amplitude ($\Delta V$) was 5 mV.

III. 3D BAND STRUCTURE

Figures 2(a) - (c) show the photoemission intensity map of Ba$_{0.95}$Na$_{0.05}$Ti$_2$Sb$_2$O measured with 100 eV photons at 16 K and 28 eV photons at 6 K, respectively, well into the density wave state. Combining these results, we obtained the Fermi surface in the projected two-dimensional BZ, as sketched in Fig. 2(d). The Fermi surface contains a small square-shaped electron pocket $\beta$ (and a cross-shaped electron pocket $\beta'$) together with a square-shaped intensity indicated as $\sigma$ around the BZ center $\Gamma$, a diamond-shaped hole pocket $\alpha$ together with a circular hole pocket $\alpha'$ around the BZ boundary $X$ and a square-shaped electron pocket $\delta$ together with a circular hole pocket $\zeta$ around the BZ corner $M$. As will be discussed below, $\alpha$ and $\alpha'$ ($\beta$ and $\beta'$) are actually different sections of the same Fermi surface, which is a consequence of an ARPES experiment with limited $k_z$ resolution on a band that is strongly dispersive along the $k_z$ direction, consistent with the band calculations shown in Fig. 3(i). It is clear that there are many nested Fermi segments in this multiband electronic structure.

The band dispersions along the high symmetry directions $\Gamma$-$M$ and $\Gamma$-$X$ in the projected two dimensional BZ are shown in Figs. 3(a) and (c), respectively, together with their corresponding momentum distribution curves (MDCs) shown in Figs. 3(b) and (d). Around $\Gamma$, there is a V-shaped $\beta$ band, and a W-shaped $\sigma$ band along both directions. The $\alpha$ band is also W-shaped and crosses the Fermi level ($E_F$) along the $\Gamma$-$X$ direction, but not along the $\Gamma$-$M$ direction, since it contributes a Fermi pocket surrounding $X$. Near $M$, there is a M-shaped band below $E_F$, which is assigned as $\eta$. In particular, another weak feature near $E_F$ in Fig. 3(a) is more clear in the data taken with linearly polarized light (s-polarization, as explained below) in Figs. 3(e) and (f), which is the parabolic $\delta$ band. Another band ($\zeta'$) becomes visible in the 28 eV data, as indicated in Figs. 3(g) and (h).

The corresponding parts of most of the observed bands can be found in the calculations reproduced in Fig. 3(i)[15], as indicated by the thickened curves and lables. For example, the electron-like $\delta$ band and the $\eta$ band beneath it can be easily identified in the calculated band structure. However, there are also some discrepancies. For instance, the hole-like $\zeta$ band does not exist in the calculations; its origin is yet to be determined. Similarly, the dispersion of $\sigma$ is not W-shaped along $\Gamma$-$X$ in the calculations, which might be caused by the inaccuracy in relative energy positions of various bands and additional hybridizations in the material. The comparison between the experimental and calculated band structures is shown in Fig. 3(i). It is clear that there are many nested Fermi segments in this multiband electronic structure.

To further explore the $k_z$ dependence of the electronic structure of Ba$_{0.95}$Na$_{0.05}$Ti$_2$Sb$_2$O, we conducted a photon energy dependent ARPES experiment. The exploited photon energies range from 92 eV to 140 eV, covering more than one whole BZ along the $k_z$ direction, as indicated in Fig. 4(a). The $\eta$
energies of about 107 eV and 125 eV, respectively. Based on this obvious change in the \( \eta \) band, we plot the MDCs at 100 meV below \( E_F \) in Fig. 4(d). To match the periodic behavior of the \( \eta \) band along \( k_z \), a 11 eV inner potential is chosen, and consequently \( \Gamma \) and \( Z \) can be determined to correspond to the photon energies of about 107 eV and 125 eV, respectively.

The \( k_z \) dispersions of all the bands that cross \( E_F \) (\( \alpha/\alpha' \), \( \beta \), \( \sigma \) and \( \delta \)) are plotted in Figs. 4(c)-4(g). For the \( \alpha/\alpha' \) band in Fig. 4(e), the MDC of \( \alpha \) is quite sharp at the \( \Gamma \) point (107 eV), and becomes quite broad around the \( Z \) point (125 eV), then back to a sharp peak around \( \Gamma \) (140 eV) in the next BZ. This variation of the broadening of the \( \alpha \) band matches the period of the BZ well. In the region where the peak of \( \alpha \) band becomes broad, there are intensities of \( \alpha' \) besides those of \( \alpha \). The existing both \( \alpha \) and \( \alpha' \) bands are in contrast with the calculations, where there is only one band around \( X \) [Fig. 3(i)]. However, because \( \alpha \) exhibits strong \( k_z \) dependence, this can be understood by considering the poor \( k_z \) resolution of our photoemission experiment. That is, the \( \alpha \) and \( \alpha' \) bands actually originate from the same band with a strong \( k_z \) dependence, thus the projection of features at other \( k_z \) results in the coexisting \( \alpha \) and \( \alpha' \) bands across the entire \( k_z \) range [16]. This holds true for \( \beta \) and \( \beta' \) bands (data of \( \beta' \) bands were not showed). Although \( \alpha \) and \( \eta \) show strong 3D nature, other bands are more 2D-like. \( \zeta \) bands [Fig. 4(c)] show little \( k_z \) dependence while almost no \( k_z \) dependence can be detected for the \( \sigma \) [Fig. 4(f)] and \( \delta \) bands [Fig. 4(g)]. The quasi-2D nature of these bands is consistent with the theoretical calculations of BaTi\(_2\)Sb\(_2\)O.

### IV. Orbital Characters of the Bands Near \( E_F \)

In both the calculations and our ARPES data, it is clear that Ba\(_{0.95}\)Na\(_{0.05}\)Ti\(_2\)Sb\(_2\)O is a multiband system. Its electronic configuration is 3\( d \)\(^1\) for the Ti\(^{3+}\) ion, and multiple orbitals would participate in the low energy electronic structure. To further demonstrate the orbital characters of the bands, we have conducted polarization dependent ARPES experiments. The geometry of the photoemission experiment setup is shown in Fig. 5(a), where the path of the incident photon beam and the sample surface normal defines the mirror plane. The \( p \) and \( s \) polarization of the light and the \( k_x \) and \( k_y \) directions of the sample are indicated in Fig. 5(a). With this experimental setup, the even (odd) \( d \) orbitals illustrated in Fig. 5(b) should be visible in \( p \) (s) geometry [17].

Figures 5(c)-(d) show the high symmetric photoemission intensity along the \( \Gamma-M, \Gamma-X \) directions under \( p \) and \( s \) polarizations, respectively. As summarized in Table I, the observed polarization dependence generally agrees with the calculated orbital characters of various bands [9]. More specifically, one finds that the \( \sigma \) band only shows up under \( p \) geometry along the \( \Gamma-M \) direction, indicating that it is composed of even orbitals in this direction [see Fig. 5(c)], which is consistent with the corresponding calculations. There is some residual intensity of the \( \beta \) band in Fig. 5(c), which might be caused by poor \( k_z \) resolution. Similarly, the projections of \( \sigma \) from other \( k_z \)'s
They generally explain the observed polarization dependence. However, there is no corresponding odd orbitals in the \( \alpha \) calculations. Also the experimental data instead along the \( Z \) plane are also largely the same as those in the \( \Gamma \) plane. Thus, the geometry. Thus, the consistency with the calculated \( d \) and \( s \) orbital characters.

In Figs. 5(e)–5(f), we present the polarization dependent photoemission intensity along the \( Z-A \) and \( Z-R \) directions. The various bands here show almost the same polarization dependence as along \( \Gamma-M \) and \( \Gamma-X \) directions, respectively. As summarized in Table 1, the calculated orbital characters in the \( Z \) plane are also largely the same as those in the \( \Gamma \) plane, and they generally explain the observed polarization dependence.

One also finds that there are some discrepancies between the data and the calculations. In particular, \( \sigma \) band is clearly present in the data taken with \( s \)-polarization along the \( Z-R \) direction, however, there is no corresponding odd orbitals in the calculations. Also the \( \alpha \) band, exhibiting odd orbital character according to calculation, is found in our \( p \)-polarized experimental data instead along the \( Z-R \) direction. These need further investigations, including further analysis using Bloch wavefunctions [17]. Nevertheless, the general agreement between the experiment and calculations suggests that the low-lying electronic bands, which are responsible for both the CDW and superconductivity, arise mainly from the Ti 3d states.

V. CHARGE DENSITY WAVE STATE

We now search for the electronic structure signature of the CDW state of Ba\(_{0.95}\)Na\(_{0.05}\)Ti\(_2\)Sb\(_2\)O. For a conventional CDW ground state, the scattering of electrons between the nested Fermi surfaces effectively drives the system into an ordered ground state. Consequently, a CDW gap opens at \( E_F \). For example, gap opening at the Fermi surface has been reported in 1T-structured TaS\(_2\) [18]. However, for 2H-structured TaS\(_2\), there is no CDW gap at the Fermi surface, instead, partial gap opening has been observed over the Fermi patches. The CDW vector match is fulfilled through participation of all the states in the Fermi patches [18]. This behavior has been observed in the density wave state of BaTi\(_2\)As\(_2\)O as well [6]. Furthermore, it has been shown in NbSe\(_2\) that the collective contribution of the weakly occupied states can dominate the CDW formation [19]. Therefore, one needs to study the temperature depen-
TABLE I: Comparison between the polarization-dependent APRES measurements in \( p \) and \( s \) geometries, and the calculated orbital characters of the bands along four high symmetry directions [15].

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- \( \alpha \sqrt{d_{x^2-y^2}} \)
- \( \beta \sqrt{d_{x^2-y^2}} \)
- \( \sigma \sqrt{d_{x^2-y^2}} \)
- \( \delta \sqrt{d_{x^2-y^2}} \)
- \( \eta \sqrt{d_{x^2-y^2}} \)

Experiment | Calculation
--- | ---
\( Z-A \) | \( Z-R \) | \( Z-A \) | \( Z-R \)
\( p \) | \( s \) | \( p \) | \( s \) | \( p \) | \( s \) | \( p \) | \( s \)

- \( \alpha \sqrt{d_{x^2-y^2}} \)
- \( \beta \sqrt{d_{x^2-y^2}} \)
- \( \sigma \sqrt{d_{x^2-y^2}} \)
- \( \delta \sqrt{d_{x^2-y^2}} \)
- \( \eta \sqrt{d_{x^2-y^2}} \)

FIG. 6: (Color online) (a)-(h) Temperature dependence of the EDCs taken at the momenta 1-8 as marked in inset. To compensate for thermal broadening effects, the 70 K data have been divided by the resolution convoluted Fermi-Dirac functions and then multiplied by that of 7 K. The data were taken in the sequence of 7 K (blue curves), 70 K (red curves), and then the temperature was cycled back to 7 K (dashed curves). Data were taken at the SSRL. The shades highlight regions with noticeable temperature dependences.

FIG. 7: (Color online) More detailed temperature dependence for the data in Fig. 6, for momentum positions as labelled in the inset of Fig. 6. (a) Temperature dependence of EDCs at position 5. To compensate for thermal broadening near \( E_F \), the spectra were divided by the resolution convoluted Fermi-Dirac function at their corresponding temperatures and then multiplied by that of 7 K. (b) The temperature dependence of the spectral intensities integrated over the shaded regions of Figs. 6(a)-(e) and (h) for momentum positions 1-5, and 8, respectively, where the spectra exhibit obvious temperature dependences.
The four circled points are the lattice Bragg spots. (d) A schematic shows directed lines with the bias voltage of -100 mV. (c) The corresponding Fourier transform of panel (b), which gives the quasiparticle interference (QPI) plot. π along the (C) direction, as shown by the dashed line in panel (c). Q is (π, π). (f), (g) Two dimensional autocorrelation maps at $E_F$ [joint density-of-states $C(q, 0)$] for ARPES intensity distributions taken at 100 eV and 28 eV, respectively. (h) Schematic of the wave vector (π, π) on the Fermi surface.

$E_F$. The agreement of the 7 K data before and after thermal cycling indicates the observed spectral changes are intrinsic. For simplicity, we do not show the EDCs taken at the temperatures in between 7 K and 70 K for these momenta.

To further study the detailed temperature evolution, Fig. 7(a) shows the detailed temperature dependence of the photoemission spectrum taken at momentum position 5. With decreasing temperature from 70 K, the spectrum first exhibits a sizable enhancement and then saturates at low temperatures, while a leading-edge gap is always absent. The integrated intensity within [$E_F$-$80$ meV, $E_F$+$30$ meV] is shown in Fig. 7(b) as a function of temperature. Similar behavior has also been observed at various other momentum positions as shown in Fig. 7(b). For some momenta, there is no saturation behavior at low temperatures, but as shown by the two lines, there is a clear change of slope around the density wave transition temperature. With decreasing temperature, the intensity increases much slower below $T_{DW}$ than above it. Moreover, we note that there is an additional suppression at the lowest temperature at several momenta. The enhancement above the density wave transition temperature is unlikely due to the density wave formation. As an alternative, strong electron-phonon interactions can induce similar temperature dependence [6]. The slope decrease below $T_{DW}$ suggests that the density wave formation may be responsible for suppressing the spectral weight there.

Similar behavior has been observed in BaTi$_2$As$_2$O, that is, an additional spectral weight suppression occurs at the Fermi surface below its density wave transition temperature beyond the continuous spectral evolution with temperature over an energy range of 200-500 meV [6], which is also manifested as a slope change for the integrated spectral weight. The transition temperature of Ba$_{0.95}$Na$_{0.05}$Ti$_2$Sb$_2$O is about a quarter of that of BaTi$_2$As$_2$O (200 K), and the energy scale for the lineshape change in the latter compound is over an energy range of 30-110 meV, also about a similar fraction of that of the former compound. This intriguing scaling behavior of these two systems suggests that their density waves share similar nature, although the density wave in Ba$_{0.95}$Na$_{0.05}$Ti$_2$Sb$_2$O is much weaker. We note that these energy scales are much larger than the mean field gap size of a density wave, which is about $\Delta \sim 1.76 k_BT_{DW}$ ≈ 7 meV for Ba$_{0.95}$Na$_{0.05}$Ti$_2$Sb$_2$O. However, such a relatively large energy scale has been commonly observed in systems with strong electron-phonon interactions [18].

To reveal the nature of the density wave in Ba$_{0.95}$Na$_{0.05}$Ti$_2$Sb$_2$O, we have further conducted STM measurements. Figure 8(a) shows a typical topographical image of a 15 nm × 15 nm region measured at 4.5 K. The cleaved surface is expected to be the Ba-terminated surface, where there forms a strong 2×1 reconstruction of
Ba atoms. The differential conductance (dI/dV) mapping at \(V_g=100\) mV, which reflects the spatial distribution of local density of states (LDOS), is plotted in Fig. 8(b). One can see that a strong 2\(\times\)1 reconstruction exists in both topographic and dI/dV mappings of the Ba atoms, since about half of the Ba atoms are lost during the cleavage. This reconstruction is so strong that it hinders the observation of other weak modulations.

In order to reveal all the proper existing structural and electronic orders, the Fourier transform of the differential conductance map is shown in Fig. 8(c). The two points with strongest intensities represent the 2\(\times\)1 reconstruction of Ba atoms, and the four circle-highlighted points are from the periodicity of the atomic structure. Fig. 8(d) sketches the periodicity of Ba atoms in the first layer, Sb atoms in the second layer, and O atoms in the third layer. One should note that there are four additional points at 45\(^\circ\) to \(q_x\) or \(q_y\) [Fig. 8(c)], marked by Q. The wavevector of this periodicity is \((\pi, \pi)\), which is beyond the crystalline Bragg spots. This thus should correspond to the long-sought CDW formation.

Furthermore, to further demonstrate the contribution to the CDW instability, we calculated the weighted joint density-of-states \(C(q,0)\) of the photoemission intensity at \(E_F\), which has proven effective at identifying Fermi surface instabilities [18]. The formula is

\[
C(q,\omega) \equiv \int M(k, \vec{k} + \vec{q})A(k, \omega)A(k + \vec{q}, \omega)dk,
\]

where

\[
M = \begin{cases} 1 & \vec{k} + \vec{q}, \vec{k} \in \text{weight-suppressed region} \\ 0 & \text{otherwise} \end{cases}
\]

Ideally, one needs to integrate over the entire three dimensional BZ, however, due to experimental limitations, only several 2D maps can be taken. The resulting \(C(q,0)\) calculated for the photoemission intensity maps in Figs. 2(a) and 2(b) are shown in Figs. 8(f) and 8(g), respectively. A strong peak is observed at \((\pi, \pi)\) in Fig. 8(f). This is consistent with the \((\pi, \pi)\) wavevector found in the STM results, and the theoretical calculations [10]. Therefore the Fermi surface instability is likely the driving force of the CDW, which is contributed largely by the nested Fermi sectors as indicated in Fig. 8(e). We note that many instabilities at other \(q\)s coexist with the \((\pi, \pi)\)—for example, there is also a weak peak near \((\pi, 0)\). However, in the competition amongst various CDW instabilities, the fastest-growing instability will cause the corresponding phonon-softening, and induce static charge order.

VI. DISCUSSIONS AND CONCLUSIONS

In conclusion, we resolved low energy electronic structure of the superconducting material \(\text{Ba}_{0.95}\text{Na}_{0.05}\text{Ti}_2\text{Sb}_2\text{O}\), which is dominated by Ti \(d_{x^2-y^2}, d_{z^2}\), and \(d_{\pi}\) orbitals. We find that correlation effects are weak in this system.

We have found the first direct evidence of CDW order in this material with STM, and the ordering wavevector is \((\pi, \pi)\). The strength of the CDW is weak, so that its usual manifestation, namely band folding or a gap or spectral weight suppression, cannot be resolved in the photoemission spectra. Instead, we observe a spectral weight enhancement with decreasing temperature, which might be induced by strong electron phonon interactions. The rate of this spectral weight enhancement at low temperatures is reduced or diminished in the CDW state, which suggests that CDW may open a partial gap, but it is compensated by the overall spectral weight enhancement. The observed Fermi surface is well nested along the \((\pi, \pi)\) direction, consistent with the CDW wavevector found by STM. Moreover, the autocorrelation of the photoemission intensity, an indication of the charge instability, also exhibits a peak at \((\pi, \pi)\). This suggests that the Fermi surface instability is the driving force behind the CDW in \(\text{Ba}_{0.95}\text{Na}_{0.05}\text{Ti}_2\text{Sb}_2\text{O}\).

The observed weak correlation and the CDW suggest that electron-phonon interactions, rather than spin fluctuations, underpin superconductivity in \(\text{Ba}_{0.95}\text{Na}_{0.05}\text{Ti}_2\text{Sb}_2\text{O}\). On the other hand, compared with other titanium pnictide oxides, the CDW affects the electronic structure of \(\text{Ba}_{0.95}\text{Na}_{0.05}\text{Ti}_2\text{Sb}_2\text{O}\) much more weakly. In fact, the spectral intensity at the Fermi energy is not reduced at low temperatures due to an underlying global enhancement. Since the CDW is expected to compete with superconductivity, the weak CDW here might be the reason why superconductivity found so far only in \(\text{Ba}_{1-x}\text{Na}_x\text{Ti}_2\text{Sb}_2\text{O}\) and not in the other other titanium pnictide oxides. One may expect superconductivity when CDW order is further reduced in other systems by certain means. Our results pave the way for further understanding of the superconductivity and the CDW in this class of systems.

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For practical purposes, atomic orbitals, instead of Bloch wavefunctions, are used for the symmetry analysis, but they usually give the same results.

