Camelback-shaped band reconciles heavy-electron behavior with weak electronic Coulomb correlations in superconducting TlNi2Se2

N. Xu,1,2,* C. E. Matt,1,3 P. Richard,4,5 A. van Roekeghem,6,8 S. Biermann,6,7,8 X. Shi,1,4 S.-F. Wu,4 H. W. Liu,4 D. Chen,4 T. Qian,4 N. C. Plumb,1 M. Radović,1,9 Hangdong Wang,10 Qianhui Mao,10 Jianhua Du,10 Minghu Fang,10,11 J. Mesot,1,2,3 H. Ding,4,5 and M. Shi1,11

1Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
2Institute of Condensed Matter Physics, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
3Laboratory for Solid State Physics, ETH Zürich, CH-8093 Zürich, Switzerland
4Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
5Collaborative Innovation Center of Quantum Matter, Beijing, China
6Centre de Physique Théorique, École Polytechnique, CNRS-UMR7644, 91128 Palaiseau, France
7Collège de France, 11 place Marcelin Berthelot, 75005 Paris, France
8Kavli Institute for Theoretical Physics, University of California, Santa Barbara, California 93106, USA
9SwissFEL, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
10Department of Physics, Zhejiang University, Hangzhou 310027, China
11Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China

(Received 22 December 2014; published 24 August 2015)

Combining photoemission spectroscopy, Raman spectroscopy, and first-principles calculations, we characterize superconducting TlNi2Se2 as a material with weak electronic Coulomb correlations leading to a bandwidth renormalization of 1.4. We identify a camelback-shaped band, whose energetic position strongly depends on the selenium height. While this feature is universal in transition metal pnictides, in TlNi2Se2 it lies in the immediate vicinity of the Fermi level, giving rise to a pronounced van Hove singularity. The resulting heavy band mass resolves the apparent puzzle of a large normal-state Sommerfeld coefficient [H. Wang et al., Phys. Rev. Lett. 111, 207001 (2013)] in this weakly correlated compound.

DOI: 10.1103/PhysRevB.92.081116 PACS number(s): 74.70.Xa, 71.20.—b, 74.25.Jb, 79.60.—i

The discovery of high-temperature superconductivity in iron-chalcogenide A1Fe2−xSex (A = Ti, K, Cs, Rb) [1,2] has raised a lot of attention because their unique Fermi surface (FS) topology without hole pocket [3–8] challenges the electron-hole quasinesting scenario as the main Cooper pairing force in the Fe-based superconducting materials [9]. However, due to the phase separation associated with Fe vacancy ordering [10,11] in A1Fe2−xSex, it is still unclear whether superconductivity in this compound is related to that of the other iron-based superconductors. Very recently, it has been found that the isostructural material TlNi2Se2 with two more electrons on the 3d shell shows superconductivity with $T_c = 3.7$ K [12]. In contrast to A1Fe2−xSex, x-ray diffraction results indicate that this system is homogeneous without Ni vacancy or phase separation, and stoichiometric TlNi2Se2 was confirmed by energy dispersive x-ray spectroscopy [12]. A large normal-state Sommerfeld coefficient has been attributed to heavy fermion behavior [12], and its square root relationship with magnetic field in the mixed state suggests d-wave pairing symmetry. On the other hand, thermal conductivity measurements suggest multiple nodeless superconducting gaps [13]. Therefore, it is crucial to determine the electronic structure of TlNi2Se2 to understand the nature of the reported heavy fermions in this material and to establish possible connections with other unconventional superconductors.

In this Rapid Communication, we present high-resolution angle-resolved photoemission spectroscopy (ARPES) results on TlNi2Se2. Photon energy dependent measurements reveal that the electronic structure exhibits three dimensionality, with four bands crossing the Fermi level ($E_F$). Our density functional theory (DFT) calculations, renormalized by a factor of 1.4, match the experimentally determined band structure very well, indicating weaker correlation effects in TlNi2Se2 than in its cousin A1Fe2−xSex [3]. We reveal that the flat top of one of the bands ($\gamma$) exhibits an asymmetric back-bending feature resulting in a camelback shape near $E_F$ at $k = (0,0,\pi)$, the $Z$ point of the first Brillouin zone (BZ). This shape is captured by our DFT calculations and seems to be a general feature of transition-metal pnictides [14]. This $\gamma$ band forms four small FS lobes around the Z point, and between the lobes four flat parts resulting in a van Hove singularity (VHS) near $E_F$ are identified. This finding provides a natural explanation to the heavy-electrons feature inferred from electronic specific heat and the upper critical field measurements [12] in this weakly correlated system. Indeed, in TlNi2Se2 $\gamma$ takes on a value of 40 mJ/mol K$^2$, which is six times larger than that of BaFe2As2 (5.6 mJ/mol K$^2$) with stronger correlations (renormalization factor $\sim 3$ [15]).

Large single crystals of TlNi2Se2 were grown by the self-flux method [12]. ARPES measurements were performed at SIS beamline of Swiss Light Source, and at the one-cubed ARPES end station of BESSY with circular polarized photons ranging 20–70 eV. The angular and energy resolutions were set to 0.2° and 5–10 meV, respectively. Clean surfaces for the ARPES measurements were obtained by cleaving crystals.
in situ in a working vacuum better than $5 \times 10^{-11}$ Torr. We label the momentum ($k$) values with respect to the 1 Ni/unit cell BZ, with the high symmetry points defined in Fig. 1(a). The Fermi level of the samples was referenced to that of a gold film evaporated onto the sample holder. Raman data have been recorded at room temperature using a 514.5 nm laser source and the single mode of a Horiba Jobin Yvon-T64000 micro-Raman spectrometer equipped with a CCD camera.

The Raman spectra in Fig. 1(b) show one $A_{1g}$ mode (177.9 cm$^{-1}$) and one $B_{1g}$ (132.8 cm$^{-1}$) phonon, similar to the observation on the isostructural 122-ferropnictides [16]. As illustrated in the inset, the intensity of these peaks is in perfect concordance with the fourfold symmetry of the crystal and the spectra are exempt of extra modes, which suggests that our TlNi$_2$Se$_2$ samples are not phase separated and do not show Ni vacancy ordering, in agreement with a previous study on KNi$_2$Se$_2$ [17].

Figure 1(c) shows the wide-energy photoemission spectra of TlNi$_2$Se$_2$. Clear double-peak features due to spin-orbit interaction are identified for states of Se 3d at binding energies ($E_B$) = 54.0 and 54.9 eV, Tl 5d at $E_B = 12.9$ and 15.1 eV, and Ni 3p at $E_B = 66.3$ and 67.9 eV (as shown in the inset). In Fig. 1(d), we plot the DFT band structure calculated for the experimental lattice parameters [12] and the height of Se from the Ni layer ($z_{Se}$) = 0.355 Å. Four bands cross $E_F$ and exhibit non-negligible three dimensionality. The density of states (DOS) near $E_F$ is contributed mainly by the Ni 3d states with a partial Se 4$p$ spectral weight. (e) DOS from DFT calculations.

FIG. 1. (Color online) (a) Two adjacent BZs of TlNi$_2$Se$_2$. (b) Raman spectra recorded under several polarization configurations [18]. (c) Core level spectra of TlNi$_2$Se$_2$ recorded with 150 eV photons. The inset is a close-up of the valence band near $E_F$.

the Fermi level of the samples was referenced to that of a gold film evaporated onto the sample holder. Raman data have been recorded at room temperature using a 514.5 nm laser source and the single mode of a Horiba Jobin Yvon-T64000 micro-Raman spectrometer equipped with a CCD camera.

The Raman spectra in Fig. 1(b) show one $A_{1g}$ mode (177.9 cm$^{-1}$) and one $B_{1g}$ (132.8 cm$^{-1}$) phonon, similar to the observation on the isostructural 122-ferropnictides [16]. As illustrated in the inset, the intensity of these peaks is in perfect concordance with the fourfold symmetry of the crystal and the spectra are exempt of extra modes, which suggests that our TlNi$_2$Se$_2$ samples are not phase separated and do not show Ni vacancy ordering, in agreement with a previous study on KNi$_2$Se$_2$ [17].

Figure 1(c) shows the wide-energy photoemission spectra of TlNi$_2$Se$_2$. Clear double-peak features due to spin-orbit interaction are identified for states of Se 3d at binding energies ($E_B$) = 54.0 and 54.9 eV, Tl 5d at $E_B = 12.9$ and 15.1 eV, and Ni 3p at $E_B = 66.3$ and 67.9 eV (as shown in the inset). In Fig. 1(d), we plot the DFT band structure calculated for the experimental lattice parameters [12] and the height of Se from the Ni layer ($z_{Se}$) = 0.355 Å. Four bands cross $E_F$ and exhibit non-negligible three dimensionality. The density of states (DOS) near $E_F$ is contributed mainly by the Ni 3d states with a partial Se 4$p$ spectral weight. (e) DOS from DFT calculations.

FIG. 1. (Color online) (a) Two adjacent BZs of TlNi$_2$Se$_2$. (b) Raman spectra recorded under several polarization configurations [18]. (c) Core level spectra of TlNi$_2$Se$_2$ recorded with 150 eV photons. The inset is a close-up of the valence band near $E_F$. (d) DFT band structure plotted along high symmetry lines. The bands near $E_F$ are colorized differently for a better visualization, and the linewidth indicates the Se 4$p$ spectral weight. (e) DOS from DFT calculations.

In Figs. 2(a) and 2(b), we plot normal emission ARPES intensities as a function of photon energy and their corresponding energy distribution curves (EDCs). Clear periodic variations of peak positions, especially for the $\gamma$ band near $E_F$ and the $\epsilon$ band at $E_B \sim 1.2$ eV, are observed with tuning the $k_z$ value by changing the photon energy, indicating strong three-dimensionality of the band structure in TlNi$_2$Se$_2$. Using the nearly-free electron approximation with an inner potential of 17 eV, we estimate $h\nu = 34$ eV for the $k_z = 0$ plane, and $h\nu = 29/54$ eV for the $k_z = \pi$ planes. We plot the ARPES intensity along the $\Gamma$-M-$Z$-$M$ momentum path, with renormalized DFT. (h) Near-$E_F$ zoom along the $\Gamma$-X direction. (i) Same as (h), with the location in $k$ space illustrated by the yellow arrow in Fig. 3(c).
and $\delta$ electronic pockets located at the $M$ point in BaFe$_2$As$_2$ are more than half filled in TlNi$_2$Se$_2$ and form holelike pockets at the $\Gamma$ point. One flat band ($\gamma$) sits $\sim 250$ meV below $E_F$ in TlNi$_2$Se$_2$, which is also observed near $E_F$ in BaCo$_2$As$_2$ [20,21]. Besides all these states, the additional $\zeta$ band is observed in TlNi$_2$Se$_2$ around the $M$ point. Our ARPES data suggest that TlNi$_2$Se$_2$ shares a universal band structure with BaFe$_2$As$_2$ and BaCo$_2$As$_2$, with a chemical potential shifted due to more 3$d$ electrons in TlNi$_2$Se$_2$ (3$d^{1.5}$) than in BaFe$_2$As$_2$ (3$d^6$) and BaCo$_2$As$_2$ (3$d^7$). This is indeed what is expected from our DFT calculations, which match the experimental data very well with a renormalization factor of 1.4 as seen in Figs. 2(c) and 2(d). TlNi$_2$Se$_2$ can thus be viewed as a heavily electron doped TiFe$_2$Se$_2$ as a first approximation. Therefore, we suggest that TiFe$_2$Se$_2$, the phase without vacancy ordering, is the superconducting compound of the iron-chalcogenide TlFe$_2$Se$_2$ (renormalization factor of 1.4) as compared to TiFe$_2$Se$_2$ (renormalization factor of 2.5 [3]) is anticipated due to the increased filling of the electronic 3$d$ shell. Indeed, the stronger correlations in BaFe$_2$As$_2$ as compared to BaCo$_2$As$_2$ are driven by the lower band filling in the presence of strong Hund’s coupling [20]. The mass enhancement due to correlation effects in TlNi$_2$Se$_2$ is much smaller than that deduced from the Sommerfeld coefficient [12]. Here we suggest the large Sommerfeld coefficient to be related to the flat band near the chemical potential at the $Z$ point. As seen from the result in Fig. 4(c) and the corresponding EDC plot in Fig. 4(g), which is recorded at $T = 5$ K, the top of the $\gamma$ band sits at the $S$ point, $\sim 2$ meV below the $E_F$ along the $Z$-$X$ direction [C1 in Fig. 4(a)], and bends back with the band bottom at $\sim 18$ meV below the $E_F$ [indicated by the EDC taken at the $Z$ point shown in the inset of Fig. 4(g)]. Along the $Z$-$M$ direction [C2 in Fig. 4(a)], the band top of $\gamma$ is slightly above $E_F$, leading the $\gamma$ band to double-cross $E_F$ and forming small lobes. The $\gamma$ band top along $Z$-$M$ is estimated at $\sim 15$ meV above $E_F$ from the high-temperature data (150 K) divided by the Fermi function shown in Fig. 4(i). In Fig. 4(e), we plot the ARPES intensity along the momentum path passing through the $S$ point and perpendicular to the $Z$-$X$ direction [C3 in Fig. 4(a)]. The corresponding EDC plot is also shown in Fig. 4(b). The $\gamma$ band crosses $E_F$ four times (passing through two small holelike lobes), and has a negative curvature at the $S$ point along C1, as seen from Fig. 4(e), and the extracted band structure in Fig. 4(f). At the same time, the $\gamma$ band has a positive curvature at the $S$ point along the perpendicular direction C1 as shown in Figs. 4(c) and 4(d). Therefore, our data confirms the picture discussed before and, in particular, the camelback shape and the VHS at the $S$ points. This can be better visualized in the band structure plotted in Fig. 4(b). In fact, this VHS is guaranteed by the asymmetry of the back-bending feature as shown in Fig. 4(c) and the extracted band structure in Fig. 4(d) along the $X$-$Z$-$M$ direction.
The existence of VHS very close to \( E_F \), provides a natural explanation for the large Sommerfeld coefficient in this weakly correlated system TlNi\(_2\)Se\(_2\). In the meantime, the FS topology of the \( \gamma \) band changes dramatically when slightly tuning the chemical potential due to the VHS, as indicated in Fig. 4(j), I–IV. When we put the chemical potential \( > 15 \) meV above \( E_F \), only the \( \delta \) band crosses at the \( Z \) point and forms a holelike pocket. By putting the chemical potential at \( 2 \) meV \( > E_B > -15 \) meV, the \( \gamma \) band crosses the chemical potential but only along the \( Z-M \) directions, forming four small holelike lobes. When the chemical potential is setting in the range of \( 17 \) meV \( > E_B > 2 \) meV, the \( \gamma \) band crosses the chemical potential twice, both along the \( Z-M \) and \( Z-X \) directions, forming a small electronlike pocket inside a concentric holelike pocket. Further shifting the chemical potential down to \( E_B > 17 \) meV, the inner electron pocket disappears, leaving two holelike pockets at the \( Z \) point. All these Lifshitz transitions associated with VHS happen with the chemical potential varying by less than 30 meV, providing a possible explanation for why \( T_c \) of KNi\(_2\)Se\(_2\) (\( \sim 0.8 \) K) [22] is \( \sim 4 \) times smaller than that of TlNi\(_2\)Se\(_2\). Because K is much more sensitive to air than Tl, a slight shift of chemical potential in KNi\(_2\)Se\(_2\) is expected. The difference of DOS near \( E_F \) due to this small chemical potential variation cannot explain \( \sim 4 \) times smaller \( T_c \) in KNi\(_2\)Se\(_2\). Most interestingly, since the strength of the hybridization of Ni-\( d_{xy} \) with the Se-\( p_z \) orbital controls the position of the saddle point with respect to \( E_F \), the FS topology is highly sensitive to the height of the selenium atom over the Ni-Se plane. This may be related to the sudden \( T_c \) drop under pressure recently reported in TlNi\(_2\)Se\(_2\) [23].

It is worth mentioning that the end member of the hole-doped BaFe\(_2\)As\(_2\), the iron pnictide KFe\(_2\)As\(_2\), shows some similarities with TlNi\(_2\)Se\(_2\). A large Sommerfeld coefficient (\( \sim 94 \) mJ/mol K\(^2\)) [24] and nodal superconductivity have been reported in KFe\(_2\)As\(_2\) [25–28] and Ba\(_{0.1}\)K\(_{0.9}\)Fe\(_2\)As\(_2\) [29]. A similar pressure effect has also been observed in KFe\(_2\)As\(_2\) [26] and TlNi\(_2\)Se\(_2\) [23] and recently a VHS has been observed in KFe\(_2\)As\(_2\) [30]. The VHS observed in the present work not only reconciles heavy-electron behavior with weak electronic Coulomb correlations in superconducting TlNi\(_2\)Se\(_2\), but also serves as a key to understand the unconventional properties in nickel- and iron-pnictide superconductors.

This work was supported by the Swiss National Science Foundation (Grant No. 200021-137783), the Sino-Swiss Science and Technology Cooperation (Project No. IZLCCZ12138954), and MOST (Grants No. 2010CB923000, No. 2011CBA001000, No. 2011CBA001012, No. 2012CB821403, and No. 2013CB921703) and NSFC (Grants No. 1104322, No. 11034011/A0402, No. 11234014, and No. 11274362) from China, the National Science Foundation under Grant No. NSF PHY11-25915, IDRIS/GENCI Orsay under Project No. 091393, and the European Research Council under Project No. 617196. The work in ZJU was supported by the Natural Science Foundation of China (Grants No. 11374261 and No. 11204059), and the National Basic Research Programs of China (Grants No. 2011CBA00103, No. 2012CB821404, and No. 2015CB921004).

[18] Here $x'$ and $y'$ are parallel to the Ni-Ni bonding while $x$ and $y$ are at 45$^\circ$ from these axes. The inset shows the evolution of the Raman intensity of the $B_{1g}$ mode as a function of the angle between the incident polarization $e_x$ and the $x$ axis, for $e_y$ parallel and perpendicular to the scattered light polarization $e_{xy}$.