Electronic structure of ZrTe$_3$

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Abstract

The Fermi surface topology of the layered superconducting charge density wave compound ZrTe$_3$ is investigated by angle resolved photoelectron spectroscopy and density functional theory. The Fermi surface is dominated by bands originating from two perpendicular systems of quasi onedimensional chains. Nesting and opening of a pseudogap at temperatures as high as 250 K are signatures of a Peierls transition in one of these chains. The nesting properties are also studied for high pressure simulated crystal structure.

Keywords: Transition metal alloys and compounds; Fermi surface

1. Introduction

ZrTe$_3$ is the only metallic compound among the transition metal trichalcogenides of the ZrSe$_3$ structure type [1–3]. Its layered crystal structure (Fig. 1 a) with monoclinic $P\overline{2}_1/m$ symmetry consists of bi-capped trigonal columns formed along the $b$ crystallographic direction [4]. Zr atoms form chains inside the prisms. Te atoms noted as Te(2) and Te(3) situated on the prism edges build another chains along the $a$ lattice vector. The first Brillouin zone for ZrTe$_3$ is shown in the Fig. 1 b.

Two phase transitions were reported for ZrTe$_3$ system; the first one to charge density wave (CDW) modulation at 63 K [5] and the second one to superconductivity at $T_c = 2 \text{ K}$ [6]. Below $T_c$ superconducting filaments along the $a$ crystallographic direction appear. The transition to CDW state was found by electron diffraction, and the modulation vector was $q_{\text{CDW}} = 0.071a^* + 0.336c^*$ (equivalent to $q_{\text{CDW}} = 0.929a^*+0.664c^*$) [5]. At the transition to CDW state electrical resistivity exhibits anomalies for $a$ and $c^*$ components [1]. The absolute value of the Hall coefficient increases on cooling through the transition temperature [1].

The effect of pressure reveals an interesting nature of a coexistence between CDW and superconductivity [7]. For the pressure increasing to 1 GPa CDW is enhanced while superconductivity is suppressed. Between 1 GPa and approximately 4.5 GPa uniquely CDW exists and for pressures higher than 5 GPa only the superconducting phase is observed.

The previous band structure calculations showed that the bands related to Te(2) and Te(3) chains form nested parts of the Fermi surface (FS) [3,8]. The angle resolved photoelectron spectroscopy (ARPES) delivered new data on the ZrTe$_3$ band structure [9,10]. The recent results [10] revealed that a pseudogap appears in the nested bands below 200 K.

To get a better insight into the phenomena, related to CDWs formation and their coexistence with superconductivity, ARPES measurements combined with band structure calculations were undertaken.

2. Experimental

ZrTe$_3$ was synthesized by reacting pure Zr and Te in evacuated silica tubes at 830° C for 7 days. The crystals were grown by a transport reaction between 660° C and 590° C during 27 days, with $I_2$ transport agent. The crystals were
The crystallographic structure of ZrTe$_3$. Indicated are the van der Waals gap (vdW) and a trigonal prismatic column. (b) Brillouin zone of ZrTe$_3$ with high symmetry points.

cleaved in situ perpendicularly to the $c^*$ direction at a pressure of $10^{-10}$ mbar. Experiments were performed by a modified VG ESCALAB spectrometer [11] using a monochromatised He $I_α$ (21.2 eV) radiation in a vacuum of $10^{-10}$ mbar. The energy and angular resolution were 25 meV and 0.5°, respectively. For the determination of the Fermi surface (FS), the polar (θ) and azimuthal (ψ) orientations of the sample were scanned between 0–78° and 0–360°, respectively, while the spectral intensity at the Fermi energy ($E_F$) was recorded. First principle calculations were performed in the framework of density functional theory (DFT) using the full potential augmented plane waves + local orbitals (APW +lo) method within the generalized gradient approximation (GGA) as implemented in the Wien2k code [12]. Structure relaxation was carried out using the ABINIT package [13,14] with relativistic separable dual-space Gaussian pseudopotentials [15] in conjunction with the local density approximation (LDA).

3. Results and discussion

Fermi surface maps (FSMs) of ZrTe$_3$ were measured both at room temperature (RT) and at 20 K (Fig. 2 a and b). The normal emission direction points along $c^*$. Band structure mapping performed along important crystallographic directions confirm the determined FS. We have also calculated the band structure of ZrTe$_3$ within both the APW+lo and the pseudopotential approach. Results from these two methods are in excellent agreement. The present calculations are also qualitatively in agreement with those obtained by Stowe and Wagner [3] and Felser et al. [8]. Differences will be discussed below.

For comparison with experiment, we derived the corresponding APW +lo FSM (see Fig. 2c) within the free electron final state (FEFS) approximation [16] assuming an inner potential of $V_0 = 9$ eV and a work function of $\phi = 4$ eV.

The FS of ZrTe$_3$ consists of four sheets, numbered as in Fig. 2 c. The first striking feature in the FSM is the pair of flat horizontal sheets (bands 1 and 2) along B–D (A–E). They disperse only weakly along the $c^*$ direction. Particular crossings within these two sheets are not resolved experimentally. The character of these two electron pockets (electron filling 13% and 5%, respectively, for bands 1 and 2) is mainly Te(2) p$_x$ + Te(3) p$_x$. Consequently these two sheets can be associated with the Te(2)–Te(3) chains running along the $a$ direction. Since these sheets are formed by $\sigma^*$ antibonding p$_x$ orbitals, a particular chain is effectively decoupled from its neighboring chains, leading near $E_F$ to weak dispersion along the $b^*$ direction and strong dispersion along the $a^*$ direction, characteristic of a quasi one-dimensional system.

The second striking feature in the FSM is the undulated vertical FS manifold formed by band 3. This hole pocket (hole filling 17%) exhibits dominant Te(1) p$_x$ character and can thus be related to the chains formed by Te(1) atoms along the $b$ direction. However, since these chains are positioned inside the layer, the overlap with neighboring atoms is more significant, resulting in an increased dimensionality of this band.

Fig. 2. ARPES Fermi surface maps of ZrTe$_3$ in gray scale with darker colors corresponding to higher intensity at room temperature (a) and at 20 K (b). Vector $k_{F1}$ denotes the place with high reduction of intensity at $E_F$. (c) Calculated FSM along the FEFS.
Inside this pocket a second almost empty hole pocket (band 4) can be seen in the calculated FSM (hole filling 2%). This pocket is present in the calculated FS as almost circular closed curves around $k_F$ for certain values of $k_z$ with Zr $d_{xz} + Te(1) p_x$ character and small ellipses near the B point with Te(1) $p_y + Zr$ $d_{xy}$ character. Here our results deviate significantly from the ones obtained by Stowe and Wagner [3], since they find an additional electron pocket instead which crosses the Fermi level around the Z point, whereas the Fermi surface obtained by Felser et al. [8] consists only of the previous three bands. In our calculation the top of band 4 lies only 0.06 eV above $E_F$, whereas in the previously reported calculations, the top of the band remains below $E_F$. The band 4 is below $E_F$ in our ARPES map taken along $\Gamma - Y (Z-C)$ (not shown), which was however obtained, for unknown $k_z$ value.

The shapes of bands 1 and 2 confirm that they form nested parts of FS, what is in general agreement with the earlier calculations [3,8]. The low temperature FSM shows that the intensity observed at the nested parts is weakened on cooling (see Fig. 2b). This reduction of spectral weight is an indication that the FS is partially removed. To confirm this, we performed a temperature dependent ARPES analysis in the FS region $k_{F1}$, where the removal of intensity at low temperature appears to be most significant. It is found that a pseudogap opens at $k_{F1}$ already below 250 K, what is a similar result to that in Yokoya’s publication [10]. The measurements also revealed that for $k_{F1}$ some intensity at $E_F$ remains down to 20 K. The collected data indicate that the mechanism of the Peierls transition [17] is responsible for the existence of the CDW in the studied system. However, the pseudogap observed in the CDW state may originate from imperfect nesting in the bands 1 and 2.

In order to study the topography of the FS as a function of pressure we relaxed the ZrTe$_3$ crystal structure at pressures of 2, 4, 6, 8 and 10 GPa using ABINIT. Since the band structures obtained from Wien2k hardly differ from the one obtained by ABINIT, we then calculated the corresponding Fermi surfaces within Wien2k. Next, we computed the static susceptibility [18,19]:

$$\chi(q) = \sum_{n,n',k} \delta(\epsilon_{n',k+q} - \epsilon_{n,k})$$

which is a measure of the FS nesting. Here $\epsilon_{n,k}$ is the band energy restricted to $E_F$, $k$ and $q$ are wave vectors and $n$ is the band index. Since the nesting vector $q_{CDW}$ is known to lie within the $a^* - c^*$ plane, the susceptibility was calculated for all $q = (q_{a^*}, 0, q_{c^*})$ values from the first Brillouin zone.

The case of $q_{a^*} = 0.92a^*$ is particularly interesting. The susceptibility curve for $q_{a^*} = 0.92a^*$ (Fig. 3) [20] contains all integrated $q_{a^*}$ values between 0.90 $a^*$ and 0.94 $a^*$, hence the experimentally observed $q_{CDW}$ vector should contribute to it. The static susceptibility for band 2 (Fig. 3a) exhibits one larger peak at $q_{a^*} = 0.13e^* - 0.33e^*$. A small peak is also visible for band 1. Both places could be related to the $q_{CDW}$ vector [21] but the peak for band 2 is more pronounced. Moreover, its height increases for 2 GPa and decreases for higher pressures, what resembles the CDW enhancement for 2 GPa and its suppression for higher pressures [7]. If the nesting is related to this peak, CDW behaviour at high pressure may be understood as an effect of FS topology.

In fact, the pressure behaviour is also closely related to superconductivity. One should keep in mind that below 63 K in the CDW state nested FS parts are not completely removed and the pseudogap is present. Also the Hall coefficient remains negative [1] indicating that the electron pockets (bands 1 and 2) still dominate in transport below the transition to the CDW state. This implies that considerable density of states (DOS) related to bands 1 and 2 remains at $E_F$ in the CDW state. It is likely that the superconducting filaments along a crystallographic direction occur in the bands having one-dimensional character in this direction, namely the bands 1 and 2. One may note that at 2 GPa, when CDW is enhanced, superconductivity is suppressed and the situation is reversed at higher pressures.

The scenario, which can be proposed, is based on a static susceptibility result for the band 2 (Fig. 3a). It assumes that at pressures, where nesting is enhanced (2 GPa) we have stronger CDWs, which remove larger part of the FS. This leads to the suppression of low temperature superconductivity due to lower DOS at $E_F$ [22]. For the pressures larger than 2 GPa nested area of the FS seems to be diminished. In consequence CDW is suppressed and because of relatively higher DOS at $E_F$ superconductivity reappears.

![Fig. 3. Static susceptibility for band 2 (a) and band 1 (b) at constant $q_{a^*} = 0.92a^*$ and $q_{c^*} = 0$ for different pressures.](image-url)
4. Conclusions

FS topology of ZrTe$_3$ was studied by means of ARPES and band structure calculations. Discussed are four bands forming the FS. Two of them, which originate from Te chains, are quasi one-dimensional along the $a$ crystallographic direction and exhibit nesting. It is proposed that both CDW and superconductivity are related to those two bands. It is also suggested that modification of the FS under high pressure changes the nested area, what has an impact on CDW and superconductivity.

References

[14] The ABINIT code is a common project of the Universite Catholique de Louvain, Corning Incorporated and other contributors (URL http://www.abinit.org).
[20] The adjacent susceptibility curve for $q_{\alpha} = 0.96a^*$ do not show any maxima, which could be related to $q_{\alpha} = 0.27a^*$ and $q_{\alpha} = 0.6a^*$ are observed. However, no special dependence on pressure was observed.
[21] The vectors $(q_{\alpha} = 0.27a^*$ and $q_{\alpha} = 0.6a^*$ ) are not equivalent in the $P 2_1/m$ space group. However, it is not obvious if the electron microscopy study from Ref. [5] could have distinguished between these two possibilities. Therefore, we treat both vectors as possible CDW modulation vectors.