Supplementary Material
Detection of surface states in quantum materials $ZrTe_2$ and TmB_4 by Scanning Tunneling Microscopy

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I. CHARACTERIZATION OF $ZrTe_2$

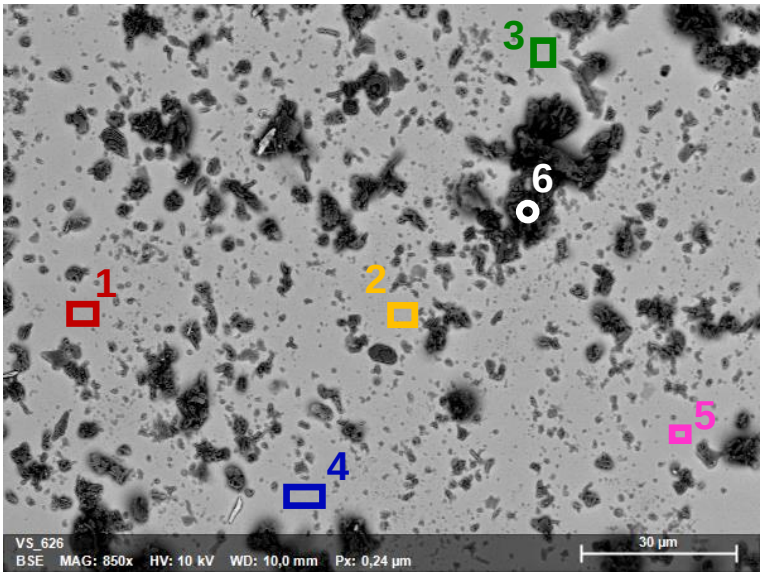

FIG. S1. Surface (not cleaved) of a single crystal $ZrTe_2$ investigated by energy dispersive X-ray spectroscopy (EDX). The markers indicate the areas within which the results presented in Table S1 were obtained. Area 6 (white) is located on an impurity phase (Zr_2Te) likely situated on top of the sample. The scale bar is 30 μm.

TABLE S1. Chemical compositions (in atomic %) of a $ZrTe_2$ single crystal obtained by EDX within the areas marked in Fig. S1.

number	color	Zr	Te	C	O
1	red	31.6	68.4	0.0	0.0
2	yellow	31.7	68.3	0.0	0.0
3	green	32.6	67.4	0.0	0.0
4	blue	32.1	67.9	0.0	0.0
5	magenta	31.7	68.3	0.0	0.0
6	white	64.4	35.6	0.0	0.0

II. CHARACTERIZATION OF TmB_4

Preparation of TmB_4 in single-crystalline form is a multistage process: (i) TmB_4 synthesis via borothermal reduction of a high pure metal oxide (Tm_2O_3) in a vacuum at 1900 K. (ii) Compaction of the obtained powder in the form of rods of approximately 8 mm diameter and 60 mm length. These rods are sintered at 2000 K in a vacuum. (iii) The

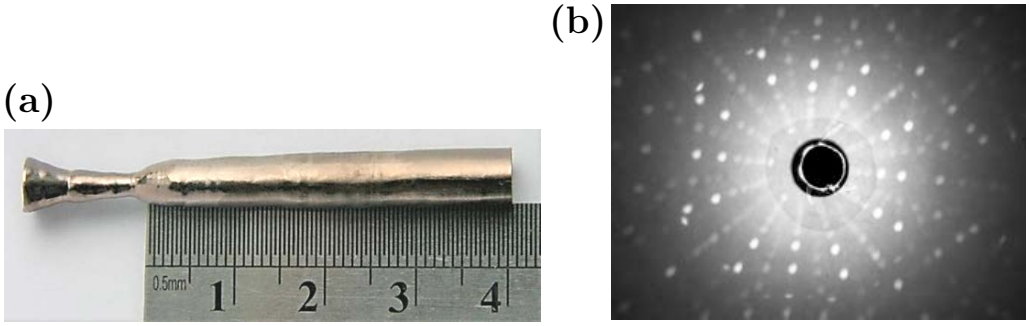

FIG. S2. Single crystal of TmB_4: (a) Photograph of an as-grown crystal. (b) X-ray Laue pattern from the cross section; deviation from the [001] crystallographic direction is about 2.5° [2].

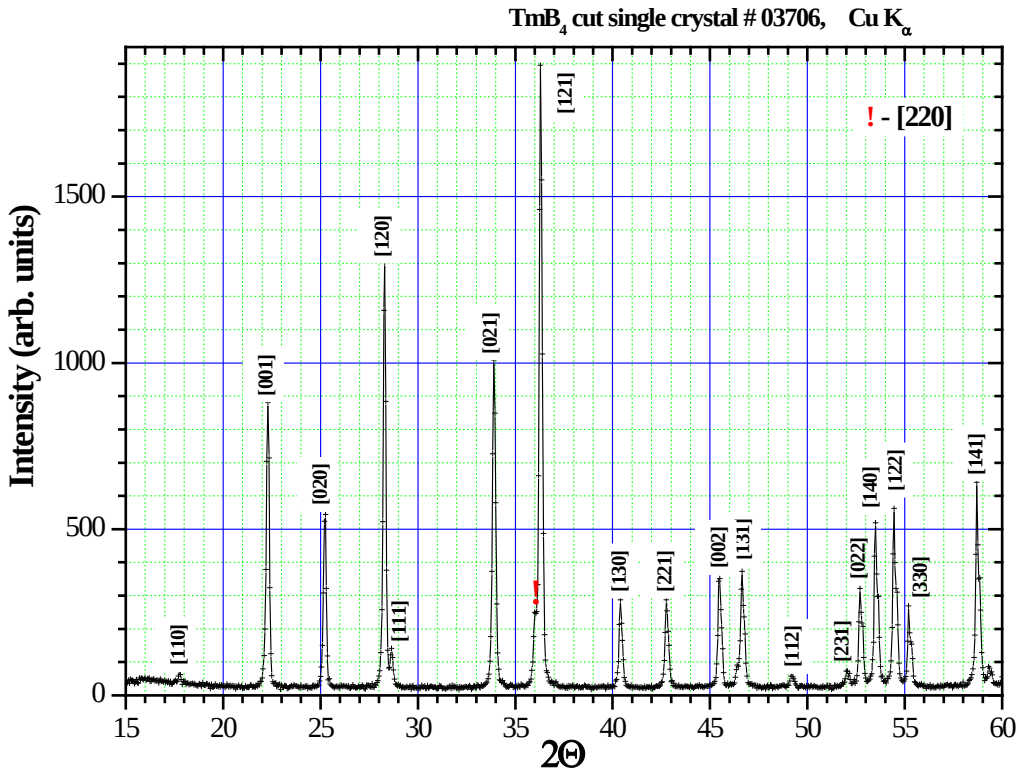

FIG. S3. Typical X-ray diffraction pattern in Cu Kα radiation obtained from crushed TmB_4 single-crystalline material as used for the preparation of the experimental samples. The lattice parameters are $a = 7.05$ Å and $c = 3.98$ Å.

use of these rods for subsequent growth of the single crystals via crucible-free zone melting with inductive heating in a closed chamber under the pressure of high-purity argon (the volume fraction of argon is no less than 99.993%). Volatile impurities in the starting boron powder are removed during the synthesis of tetraborides and in the process of zone melting, in contrast with rare-earth (RE) impurities, as the zone-refining process is not effective at reducing RE impurities [1]. Therefore, the purity of thulium oxide with respect to RE impurities is a very important factor, which can influence the Low-temperature properties of the resulting TmB_4 single crystal.

The TmB_4 single crystals were obtained with amorphous natural boron (^{nat}B: 18.83% ^{10}B, 81.17% ^{11}B, AVIABOR, Dzerzhinsk, Russia (99.9 wt.% purity) and Tm_2O_3 of purity 99.986 wt.% from the Federal State Research and Development Institute of Rare Metal Industry, Moscow, Russia) according to the product certification. Additional purification during zone melting determined the final high purity of the grown crystals such that the impurity content was less than 10^{-3} wt.% (besides RE). The RE impurities were determined by the purity of the source oxide. The presence of oxygen in the grown TmB_4 single crystals was checked using pulsed reductive extraction with carbon in a flow of helium gas (the gas chromatography). The oxygen content did not exceed 0.04 wt.%, i.e., oxygen is chemically

bound to the surface of the crushed single crystal.

A photograph of an as-grown TmB_4 single crystal is presented in Fig. S2(a) along with its Laue backscattering pattern, Fig. S2(b). The absence of splitting of the point reflections confirmed the lack of domains with a misorientation of more than several tenths of a degree (procedure accuracy). An X-ray diffraction pattern from the crushed crystal revealed reflections of the ThB_4 structure type only (Fig. S3). The parameters during the growth procedure were as follows: The source composition was stoichiometric, the growth rate was 14 mm/h in an Ar pressure of about 1 bar, and the feed rod rotation speed was 15 rpm. The [001] crystallographic direction was the primary spontaneous growth direction. The residual resistivity ratio (RRR) of this particular TmB_4 crystal was larger than 100.

[1] Tanaka, T.; Nishitani, R.; Oshima, C.; Bannai, E.; Kawai, S. The preparation and properties of CeB_6, SmB_6, and GdB_6. *J. Appl. Phys.* **1980**, *45*, 3877–3883. https://doi.org/10.1063/1.328133 (Ref. [66] of the main text).

[2] Shitsevalova, N. Crystal chemistry and crystal growth of Rare-earth borides. In *Rare-earth borides*; Inosov, D., Ed.; Jenny Stanford Publishing, Singapure, 2021; pp. 1–243. https://doi.org/10.1201/9781003146483 (Ref. [37] of the main text).