Complete surface phase diagram of IrTe$_2$ revealed by photoemission spectroscopy

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In the transition metal dichalcogenide IrTe$_2$, low-temperature charge-ordered phase transitions lead to the occurrence of stripe phases of different periodicities and nearly degenerate energies. Bulk-sensitive measurements have shown that, upon cooling, IrTe$_2$ undergoes two such first-order phase transitions at $T_{c_1} = 270$ K and $T_{c_2} = 180$ K. Here, using surface sensitive probes of the electronic structure of IrTe$_2$, we show that, in addition, another first-order transition occurs at the surface at $T_{c_1} = 165$ K. By performing measurements over a full thermal cycle, we also reveal the complete hysteresis of all these phases.

Transition-metal dichalcogenides (TMDC) are layered quasi-two dimensional (2D) materials that have generated considerable interest in recent years due to the possibility of reducing their thickness down to the monolayer as well as to their particularly diverse optical and electronic properties despite their chemical simplicity $^{[1,4]}$. Additionally, TMDCs have been extensively studied for several decades, due to the occurrence of phase transitions such as charge density waves (CDW) or superconductivity $^{[5,7]}$ at low temperatures. An open question is how these collective states evolve for thicknesses of a few layers at surfaces. Many recent examples have illustrated different behaviors in monolayers, namely an enhanced critical temperature for the CDW in TiSe$_2$ $^{[8]}$, enhanced superconductivity in TaS$_2$ $^{[9]}$, or a change in the symmetry of the CDW in VSe$_2$ $^{[10]}$. In this context, the surface of IrTe$_2$ offers an exciting new platform for studying ordered phases in a quasi-2D material with large spin-orbit coupling on the transition metal site. A complex succession of charge-ordered phases involving the creation of Ir dimers $^{[3,11,12]}$ has been observed in IrTe$_2$ at low temperature, which gives way to superconductivity for thin samples $^{[13]}$, after rapid cooling $^{[14]}$ or with Pt substitution $^{[15]}$.

IrTe$_2$ undergoes a first-order structural phase transition at $T_{c_1} = 270$ K from a trigonal CdI$_2$-type ($P\overline{3}m1$) unit cell to a monoclinic ($P\overline{1}$) unit cell accompanied by jumps in the resistivity and magnetic susceptibility $^{[1,17,18,20,24]}$. In this first low-temperature charge-ordered phase, one-dimensional stripes of Ir dimers with a strongly reduced bond length have been observed by x-ray diffraction and are described by a wave vector $(5 \times 1 \times 5)$ $^{[2,11,17,21,26,28]}$. At $T_{c_2} = 180$ K, a second phase transition follows and the charge-ordering wave vector of this new low-temperature phase is $(8 \times 1 \times 8)$ in the bulk of IrTe$_2$. This has stimulated many scanning tunneling microscopy (STM) studies, which evidenced additional ordering patterns and revealed a surface $(6 \times 1)$ periodicity proposed to be the ground state reconstruction $^{[12,17,26,29]}$. A detailed low energy electron diffraction (LEED) and STM study observed in addition the coexistence of the surface $(8 \times 1)$ and $(6 \times 1)$ phases over a wide temperature range $^{[29]}$. It was stressed that this coexistence of phases of nearly degenerate energies and of different stripe periodicities could be associated with the devil’s staircase $^{[12,20]}$.

Numerous angle-resolved photoelectron spectroscopy (ARPES) investigations have revealed large changes in the spectral weight of electronic states up to $2$ eV below the Fermi level ($E_F$) at low temperatures, leading to severe band broadening $^{[12,17,26,29,31]}$. In parallel, x-ray photoemission spectroscopy (XPS) studies have identified a large splitting of the Ir 4$f$ core level across the charge-ordered phase transitions into Ir$^{3+}$ and Ir$^{4+}$ mixed valence states $^{[17,32]}$. However, in all these surface-sensitive studies, a clear sequence of sharp transitions between the surface $(5 \times 1)$, $(8 \times 1)$ and $(6 \times 1)$ phases could not be unambiguously detected.

In this letter, we present a systematic temperature-dependent study of the electronic properties at the surface of IrTe$_2$. Using XPS, we measure the evolution of the Ir dimer density upon cooling down to $30$ K and warming back to room temperature by quantifying the Ir 4$f$ core-level peak intensities. While we confirm the sharp first-order transition occurring at $T_{c_1}$, we observe a more intricate behavior below $T_{c_2}$ at the surface. The $(5 \times 1)$ phase is replaced by the $(8 \times 1)$ phase that progressively changes into the $(6 \times 1)$ phase, indicating $(6 \times 1)$ domain growth at the expense of the $(8 \times 1)$
domains. However, our ARPES measurements reveal that a third first-order structural transition between the (8 x 1) and (6 x 1) phases occurs at $T_{c_3} = 165$ K. This is based on the observation of a surface state at about 1 eV binding energy that is an excellent marker of the periodicity of the dominating phase, since its binding energy is dictated by the Ir dimer length, as supported by density functional theory (DFT) calculations. By analyzing both XPS and ARPES data over the full warming and cooling cycle, and combining them with LEED measurements, we are able to reconstruct the complete surface phase diagram of IrTe$_2$ with the hysteretic behavior of all (5 x 1), (8 x 1) and (6 x 1) phases.

Single crystals of IrTe$_2$ were grown using the self-flux method [11,18]. They were characterized by magnetic susceptibility measurements and x-ray diffraction, which confirm that $T_{c_1} = 270$ K and $T_{c_2} = 180$ K. Samples were cleaved at room temperature in vacuum at a pressure of about 10$^{-8}$ mbar; during the photoemission measurements, the base pressure was better than 5 x 10$^{-11}$ mbar. XPS measurements were acquired at the PEARL beamline [33] of the Swiss Light Source. The total energy resolution was 190 meV. The temperature-dependent ARPES study was carried out using a Scienta DA30 photoelectron analyzer and monochromatized He$_{\gamma}$ radiation as excitation source ($h\nu = 21.22$ eV). The total energy resolution was about 5 meV and the error on the sample temperature estimated to be 5 K. Small spot LEED with micron resolution ($\mu$LEED) data were obtained using a low energy electron microscope (LEEM)/photoemission electron microscopy (PEEM)/LEED instrument (Elmitec GmbH). Samples were cleaved in ultra-high vacuum (1 x 10$^{-10}$ mbar). The aperture for LEED measurements was set to select a spatial region on the sample of 20 $\mu$m.

DFT calculations with spin-orbit interaction were performed using the Vienna ab-initio simulation package (VASP) [34–37] within the projector augmented wave method [38] and the PBE functional [39]. The cutoff energy was set to 400 eV and the k-point grid spacing ($\Gamma$) was set to select a spatial region on the sample of 20 $\mu$m. By analyzing both XPS and ARPES data over the full warming and cooling cycle, and combining them with LEED measurements, we are able to reconstruct the complete surface phase diagram of IrTe$_2$ with the hysteretic behavior of all (5 x 1), (8 x 1) and (6 x 1) phases.

We present first a detailed XPS study of the Ir 4f core levels. Fig. 1 (a) and (b) shows a zoom on the Ir 4f$_{7/2}$ core-levels measured at different temperatures upon cooling and warming, respectively. A clear splitting occurs below $T_{c_1}$, with a new peak appearing at 61.2 eV binding energy and corresponding to the Ir$^{4+}$ states (the peak at 60.6 eV binding energy is attributed to the Ir$^{3+}$ states). Across $T_{c_2}$ upon cooling (Fig. 1 (a)), the intensity ratio between the Ir$^{4+}$ and Ir$^{3+}$ peaks is reversed, and upon warming (Fig. 1 (b)), this intensity ratio changes further in a non-trivial way. In Fig. 1 (c), the intensity ratio

![FIG. 1. (Color online) XPS spectra of Ir 4f$_{7/2}$ core levels measured with a photon energy $h\nu = 200$ eV at various temperatures during (a) cooling and (b) warming. (c) Intensity ratio of the Ir$^{4+}/$(Ir$^{3+}$+Ir$^{4+}$) peaks in the Ir 4f core levels as a function of temperature. (d) Schematic description of the stripe periodicities in the Ir planes for different phases.](image-url)
over 6 Ir atoms (see Fig. 1 (d)). Interestingly, when warming the sample above 110 K, this ratio increases to 0.65, indicating further changes in the (6 × 1) vs (8 × 1) phase ratio. This effect, although small, can be directly seen on the XPS spectra of Fig. 1 (b), and will be addressed further below. In summary, upon cooling, the Ir$^{4+}$/(Ir$^{3+}$+Ir$^{4+}$) intensity ratio measured by XPS reveals that a sharp transition occurs across $T_c^1$, but that the evolution below $T_c^2$ is continuous with temperature, as a consequence of coexistence of domains with different stripe periodicities.

We have also performed ARPES measurements as a function of temperature, to discriminate further the occurrence of difference phases in IrTe$_2$. Figure 2 (a) shows its room-temperature Fermi surface (integrated over 0.05 eV around the Fermi level). At this photon energy, states close to the $ALH$ plane are probed, in agreement with the literature [42, 44]. The three-dimensional Brillouin zone and its surface projection are presented in Fig. 2 (b). In Fig. 2 (c), ARPES spectra taken at 295 K > $T_c^1$, $T_c^1$ > 200 K > $T_c^2$ and 50 K < $T_c^2$, along the $AL$ direction are displayed, together with their curvature. Corresponding energy distribution curves (EDCs) integrated around $A$ are shown in Fig. 2 (d). At 295 K (Fig. 2 (c), left panels), the electronic bands are sharp and, by comparison with the literature [43, 45], we can identify the presence of a bulk state B1 just below the Fermi level $E_F$, a surface resonance SR dispersing around 0.5 eV binding energy on top of a bulk band B2, and an intense surface state SS at about 1 eV binding energy. All these features can be seen in the corresponding EDC (Fig. 2 (d)). When decreasing the temperature below $T_c^2$, the electronic bands become intricate due to the new translational symmetry of the charge-ordered phases and their mixed orientations [3]. One distinguishes a multitude of folded bands (see Fig. 2 (c) center and right panels), especially, in the binding energy range between $E_F$ and 2.0 eV. At 200 K, in the (5 × 1) phase, the surface state is split into two states. This is more obvious in the EDC (light blue curve) in Fig. 2 (d). We attribute the surface state positioned at 1 eV binding energy (labelled SS 3) as originating from the undimerized triple Ir atoms, since it lies at the same energy as the surface state of the RT (1 × 1) phase, for which there are only undimerized atoms. The intense second surface state (labelled SS D) is shifted to about 1.3 eV binding energy and we attribute it to the dimerized Ir atoms. At 50 K, in the (6 × 1)-dominated phase (see right panels in Fig. 2 (c) and orange EDC in Fig. 2 (d)), we identify a further split sur-
face state at about 1.2 eV binding energy and attribute it to the single isolated Ir atom (SS 1) present only in the (8 × 1) and (6 × 1) phases (see Fig. 1 (d)). Additionally, the SS D surface state shifts further to higher binding energies. To support our interpretation, we have performed DFT calculations on a slab geometry for the different surface phases (see Supplementary Material for details). The shift in binding energy of the surface state in the (5 × 1) and (6 × 1) phases (with respect to the (1 × 1) case) is plotted on Fig. 2 (f) as blue and orange dashed lines, respectively, showing a very good agreement with experimental data.

Based on these observations, we consider the energy of the surface state at the highest binding energy as a marker of the phase and stripe periodicities. EDCs at different temperatures are shown in Fig. 2 (e) upon cooling (left) and warming (right) the sample. Interestingly, they exhibit a shift in energy and can be collected in different groups upon cooling, but do not show many changes upon warming. We have fitted them in the displayed energy range with a single Gaussian. The resulting surface state energy position is displayed on Fig. 2 (f) (full symbols) as a function of temperature. Three different sharp transitions can be observed upon cooling and, by comparison with the XPS data (Fig. 1 (c)), we identify the transition at $T_{c_1}$ into the (5 × 1) phase, at $T_{c_2}$ the transition into the (8 × 1) phase and at $T_{c_3} = 165$ K the transition into the (6 × 1) phase. All of them are expected to be first-order transitions, but surprisingly, we do not observe the distinct hysteresis of the (8 × 1) and (6 × 1) phases upon warming up to 240 K.

An alternative explanation is that the subsurface IrTe$_2$ layers might transit from the bulk (8 × 1) phase and lock-in to the surface (6 × 1) phase. XPS at a photon energy of 200 eV probes electronic states deeper in the sample than ARPES at 21.22 eV. Assuming a subsurface domain reorganization, it is interesting to note that there are hints of a weak transition occurring upon warming around 230 K in transport data from the literature 17 18 45, the corresponding to different structural phases observed at different temperatures. In each case, only a single phase was present within the selected real-space region. IrTe$_2$ has then been measured continuously with $\mu$LEED while heating the sample, starting from the (6 × 1)-dominated phase at about 160 K. The evolution of the contribution of the (6 × 1), (8 × 1) and (5 × 1) spots to the LEED images is shown in Fig. 3 (b). From the lowest temperature of 160 K the (6 × 1) phase remains the only phase visible until 230 K when the system transforms abruptly to the (8 × 1) phase. The (8 × 1) phase persists up to 280 K and then disappears, transiently giving way to the (5 × 1) phase, before the (1 × 1) phase sets in again.

FIG. 3. (Color online) Temperature dependent LEED spot analysis. (a) Line cuts of LEED images taken in different structural phases (at different temperatures) from a region of the sample of around 20 $\mu$m diameter. Solid markers highlight the superstructure peak positions in each phase. Curves are offset vertically for clarity. (b) Intensity in a single superstructure spot for the (6 × 1), (8 × 1) and (5 × 1) phases as a function of temperature during warming.

To investigate in more details possible changes in the stripe phases upon warming, we have performed $\mu$LEED measurements on IrTe$_2$. Line cuts through the LEED images are shown in Fig. 3 (a) revealing the surface (1 × 1) diffraction spots and the superstructure spots corresponding to different structural phases obtained at different temperatures.
temperature at which the \((6 \times 1)\) phase disappears in our data (see Fig. 3 (b)).

In this work, we have studied the surface electronic structure of \(\text{IrTe}_2\) with ARPES and XPS and have performed a detailed and systematic temperature dependent analysis across its charge-ordered phases. A new first-order transition at 165 K between the \((8 \times 1)\) and \((6 \times 1)\) phases is revealed, supporting the realization of a harmless devil’s staircase. Our work emphasizes the difference between the bulk and surface of \(\text{IrTe}_2\) and demonstrates the importance of the low dimensional environment of the surface in stabilizing charge ordered phases. This naturally stimulates more studies on thin samples and, ultimately, on a monolayer of \(\text{IrTe}_2\).

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[1] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, Nature Nanotechnology 7, 699 (2012)
[2] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, B. Hediger and O. Raetzo.
[3] K. F. Mak, K. He, J. Shan, and T. F. Heinz, Nature Nanotechnology 7, 494 (2012)
[4] R. Bertoni, C. W. Nicholson, L. Waldecker, H. Hübener, C. Monney, U. De Giovannini, M. Puppin, M. Hoesch, E. Springate, R. T. Chapman, C. Cacho, M. Wolf, A. Rubio, and R. Ernstorfer, Phys. Rev. Lett. 117, 277201 (2016)
[5] K. Rossenagel, Journal of Physics: Condensed Matter 23, 213001 (2011)
[6] M. D. Johannes and I. I. Mazin, Phys. Rev. B 77, 165135 (2008)
[7] S. Pyon, K. Kudo, and M. Nohara, Journal of the Physical Society of Japan 81, 053702 (2012)
[8] P. Chen, Y.-H. Chan, M.-H. Wong, X.-Y. Fang, M. Y. Chou, S.-K. Mo, Z. Hussain, A.-V. Fedorov, and T.-C. Chiang, Nano Letters 16, 6331 (2016)
[9] E. Navarro-Mortalla, J. O. Island, S. Manas-Valero, E. Pinilla-Cienfuegos, A. Castellanos-Gomez, J. Quereda, G. Rubio-Bollinger, L. Chirolli, J. A. Silva-Guillen, N. Agrait, G. A. Steele, F. Guinea, H. S. J. van der Zant, and E. Coronado, Nature Communications 7, 11043 (2016)
[10] P. Chen, W. W. Pai, Y.-H. Chan, V. Madhavan, M. Y. Chou, S.-K. Mo, A.-V. Fedorov, and T.-C. Chiang, Phys. Rev. Lett. 121, 196402 (2018)
[11] G. L. Pascut, K. Haule, M. J. Gutmann, S. A. Barnett, A. Bombardi, S. Artyukhin, T. Birol, D. Vanderbilt, J. J. Yang, S.-W. Cheong, and V. Kiryukhin, Phys. Rev. Lett. 112, 086402 (2014)
[12] T. Maurer, M. Vogt, P.-J. Hsu, G. L. Pascut, K. Haule, V. Kiryukhin, J. Yang, S.-W. Cheong, W. Wu, and M. Bode, Phys. Rev. B 94, 014106 (2016)
[13] P.-J. Hsu, T. Maurer, M. Vogt, J. J. Yang, Y. S. Oh, S.-W. Cheong, M. Bode, and W. Wu, Phys. Rev. Lett. 111, 266401 (2013)
[14] M. Yoshida, K. Kudo, M. Nohara, and Y. Iwasa, Nano Letters 18, 3113 (2018)
[15] H. Oiike, M. Kamitani, Y. Tokura, and F. Kagawa, Science Advances 4 (2018)
[16] S. Pyon, K. Kudo, and M. Nohara, Journal of the Physical Society of Japan 81, 053702 (2012)
[17] K.-T. Ko, H.-H. Lee, D.-H. Kim, J.-J. Yang, S.-W. Cheong, M. J. Eom, J. S. Kim, R. Gammag, K.-S. Kim, H.-S. Kim, T.-H. Kim, H.-W. Yeom, T.-Y. Koo, H.-D. Kim, and J.-H. Park, Nature Communications 6, 7342 (2015)
[18] A. F. Fang, G. Xu, T. Dong, P. Zheng, and N. L. Wang, Scientific Reports 3, 1153 (2013)
[19] S. Jobic, P. Deniard, R. Brec, J. Rouxel, A. Jouanneaux, and A. N. Fitch, Zeitschrift für anorganische und allgemeine Chemie 598, 199 (1991)
[20] N. Matsumoto, K. Taniguchi, R. Endoh, H. Takano, and S. Nagata, Journal of Low Temperature Physics 117, 1129 (1999)
[21] T. Toriyama, M. Kobori, T. Konishi, Y. Ohta, K. Sugimoto, J. Kim, A. Fujiwara, S. Pyon, K. Kudo, and M. Nohara, Journal of the Physical Society of Japan 83, 033701 (2014)
[22] S. Koley, Solid State Communications 247, 40 (2016)
[23] B. Li, G. Huang, J. Sun, and Z. Xing, Scientific Reports 4, 6433 (2014)
[24] E. Paris, B. Joseph, A. Iadecola, C. Marini, H. Ishii, K. Kudo, S. Pascarelli, M. Nohara, T. Mizokawa, and N. L. Saini, Phys. Rev. B 93, 134109 (2016)
[25] G. L. Pascut, T. Birol, M. J. Gutmann, J. J. Yang, S.-W. Cheong, K. Haule, and V. Kiryukhin, Phys. Rev. B 90, 195122 (2014)
[26] Q. Li, W. Lin, J. Yan, X. Chen, A. G. Gianfrancesco, D. J. Singh, D. Mandrus, S. V. Kalinin, and M. Pan, Nature Communications 5, 5358 (2014)
[27] Y. S. Oh, J. J. Yang, Y. Horibe, and S.-W. Cheong, Phys. Rev. Lett. 110, 127209 (2013)
[28] K. Takubo, R. Comin, D. Ootsuki, T. Mizokawa, H. Wadati, Y. Takahashi, G. Shibata, A. Fujimori, R. Sutarto, F. He, S. Pyon, K. Kudo, M. Nohara, G. Levy, I. S. Ellis-mov, G. A. Sawatzky, and A. Damascelli, Phys. Rev. B 90, 081104 (2014)
[29] J. Dai, K. Haule, J. J. Yang, Y. S. Oh, S.-W. Cheong, and W. Wu, Phys. Rev. B 90, 235121 (2014)
[30] C. Chen, J. Kim, Y. Yang, G. Cao, R. Jin, and E. W. Plummer, Phys. Rev. B 95, 094118 (2017)
[31] C. Monney, A. Schuler, T. Jaouen, M.-L. Mottas, A. Bombardi, S. Artyukhin, T. Birol, D. Vanderbilt, J. J. Yang, Y. S. Oh, S.-W. Cheong, M. Bode, and W. Wu, Phys. Rev. Lett. 111, 266401 (2013)
[32] T. Qian, H. Miao, Z. J. Wang, X. Shi, Y. B. Huang,
P. Zhang, N. Xu, L. K. Zeng, J. Z. Ma, P. Richard, M. Shi, G. Xu, X. Dai, Z. Fang, A. F. Fang, N. L. Wang, and H. Ding, *New Journal of Physics* **16**, 123038 (2014).

[33] M. Muntwiler, J. Zhang, R. Stania, F. Matsui, P. Oberta, U. Flechsig, L. Patthey, C. Quitmann, T. Glatzel, R. Widmer, E. Meyer, T. Jung, P. Aebi, R. Fasel, and T. Greber, *Journal of Synchrotron Radiation* **24**, 354 (2017).

[34] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).

[35] G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994).

[36] G. Kresse and J. Furthmueller, *Computational Materials Science* **6**, 15 (1996).

[37] G. Kresse and J. Furthmueller, *Phys. Rev. B* **54**, 11169 (1996).

[38] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).

[39] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

[40] P. V. C. Medeiros, S. Stafstroem, and J. Bjoerk, *Phys. Rev. B* **89**, 041407 (2014).

[41] P. V. C. Medeiros, S. S. Tsirkin, S. Stafstroem, and J. Bjoerk, *Phys. Rev. B* **91**, 041116 (2015).

[42] D. Ootsuki, S. Pyon, K. Kudo, M. Nohara, M. Horio, T. Yoshida, A. Fujimori, M. Arita, H. Anzai, H. Namatame, M. Taniguchi, N. L. Saini, and T. Mizokawa, *Journal of the Physical Society of Japan* **82**, 093704 (2013).

[43] D. Ootsuki, T. Toriyama, M. Kobayashi, S. Pyon, K. Kudo, M. Nohara, T. Sugimoto, T. Yoshida, M. Horio, A. Fujimori, M. Arita, H. Anzai, H. Namatame, M. Taniguchi, N. L. Saini, T. Konishi, Y. Ohta, and T. Mizokawa, *Journal of the Physical Society of Japan* **83**, 033704 (2014).

[44] D. Ootsuki, H. Ishii, K. Kudo, M. Nohara, M. Arita, H. Namatame, M. Taniguchi, N. L. Saini, and T. Mizokawa, *Journal of Physics and Chemistry of Solids* **128**, 270 (2019).

[45] H. Lee, K.-T. Ko, K. Kim, B.-G. Park, J. Yang, S.-W. Cheong, and J.-H. Park, *Europhysics Letters* **120**, 47003 (2017).

[46] M. S. Bahramy, O. J. Clark, B.-J. Yang, J. Feng, L. Bawden, J. M. Riley, I. Markovic, F. Mazzola, V. Sunko, D. Biswas, S. P. Cooil, M. Jorge, J. W. Wells, M. Leandersson, T. Balasubramanian, J. Fuji, I. Vobornik, J. E. Rault, T. K. Kim, M. Hoesch, K. Okawa, M. Askawa, T. Sasagawa, T. Eknaphakul, W. Meevasana, and P. D. C. King, *Nature Materials* **17**, 21 (2017).

[47] Formally, we do not measure electronic surface states with µLEED, but we make use of the transition temperatures (upon warming) extracted with µLEED to extrapolate the phase diagram of Fig. 2 (f).

[48] O. Ivashko, L. Yang, D. Destraz, E. Martino, Y. Chen, C. Guo, H. Yuan, A. Pisoni, P. Matus, S. Pyon, K. Kudo, M. Nohara, L. Forró, H. Romnow, M. Huecker, M. v. Zimmermann, and J. Chang, *Scientific Reports* **7**, 17157 (2017).
Supplemental material

Complete surface phase diagram of \( \text{IrTe}_2 \) revealed by photoemission spectroscopy

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DENSITY FUNCTIONAL THEORY CALCULATIONS

The electronic structure of \( \text{IrTe}_2 \) was modeled by calculating the band structure for a 4-layer slab structures for the pristine room temperature (RT) phase \([1]\), for the \((5 \times 1 \times 5)\) reconstruction and for an interpolated evolution between the RT-pristine and the \((6 \times 1 \times 6)\) reconstruction. We have taken the structural parameters of \( \text{IrTe}_2 \) \((5 \times 1 \times 5)\) and have assumed that the structural parameters in the \( \text{IrTe}_2 \) \((6 \times 1 \times 6)\) phase are the same as in \( \text{IrTe}_{(2-x)}\text{Se}_x \) \((x = 0.4)\) as in Ref. \([2]\).

In that respect, it is important to recall that the dimer bond length \( L_{\text{dim}} \) displays a significant variation as a function of temperature. Pascut et al. inferred \( L_{\text{dim}} = 3.119 \text{ Å} \) and \( 3.099 \text{ Å} \) for the \((5 \times 1 \times 5)\) and for the \((8 \times 1 \times 8)\) bulk phases, respectively, and proposed a value of \( L_{\text{dim}} = 3.005 \text{ Å} \) (confirmed experimentally in the STM study of Hsu et al. \([3]\)) for a DFT-calculated \((6 \times 1 \times 6)\) reconstruction \([2]\). The overall picture is that the Ir dimer bond length decreases across the different phases. So it is very likely that the increase of the binding energy of the surface state SS D is due to a shortening of the Ir dimer bonds. To check this idea, an interpolation parameter \( \lambda \) was introduced, with values \( \lambda = 0.0 \) and \( \lambda = 1.0 \) corresponding to the RT surface phase and the surface \((6 \times 1)\) reconstruction, respectively. To have a controlled interpolation of the structural parameters (lattice parameters and atom positions, as well as dimer length), structural relaxation was not considered. For comparison with experimental ARPES data, the surface \((6 \times 1)\) band structures were unfolded to a corresponding \((1 \times 1)\) reciprocal cell.

We have performed DFT calculations for a 4-layer slab in the \((1 \times 1)\) phase using the atomic structure proposed in Ref. \([2]\), see Fig. SM1(b), in order to understand how the energy position of the surface state (SS) is influenced by the \( \text{Ir}^{4+} \)-\( \text{Ir}^{4+} \) dimer bond length \([2]\). The surface state is very well reproduced at 1.0 eV binding energy in comparison to the experiment at RT Fig. SM1(a). The resulting band structure becomes very complicated, because of the multiplicity of the bands in the slab geometry and the \((5 \times 1)\) phase, see Fig. SM1(c). Therefore,

FIG. SM1. (a) ARPES spectrum of \( \text{IrTe}_2 \) along the \( AL \) direction at RT. (b) Density functional theory calculations for a 4-layer slab along \( \Gamma \bar{M} \) in the \((1 \times 1)\) phase (no dimerization). (c) DFT calculations for a 4-layer slab along \( \Gamma \bar{M} \) in the \((5 \times 1)\). DFT calculations for a 4-layer slab along \( \Gamma \bar{M} \) in the \((6 \times 1)\) phase for (d) \( \lambda = 0.4 \), (e) \( \lambda = 0.6 \) and (f) \( \lambda = 1.0 \) (full dimerization).
to simplify and isolate the main effect of this dimerization, we have interpolated the atomic structure between the non-dimerized and fully dimerized unit cells. The parameter $\lambda$ quantifies this continuous interpolation, with $\lambda = 0$ meaning no dimerization and $\lambda = 1$ meaning the fully dimerized ($6 \times 1$) phase. Fig. SM1 (d)-(f) shows the corresponding DFT band structure for $\lambda = 0.4$ along the $\Gamma M$ direction. In comparison to the calculations of Fig. SM1 (b), all bands are duplicated 4 times due to the 4 layers of the slab. In Fig. SM1 (d), at an intermediate dimerization ($\lambda = 0.4$), bands become back-folded to the original Brillouin zone and the unfolded band structure displays blurred bands. However, the surface state is still recognizable and shifts to higher binding energy (see red arrows). We have performed such calculations for $\lambda$ up to 1 and tracked the energy position of the surface state. The resulting values for the surface state (SS), shown in Fig. 2 (f) of the main text, compare very well with the experimental data. In particular, it reproduces the shift in the surface state (SS) as a function of the dimer increase for the ($5 \times 1$) reconstruction and the fully dimerized ($6 \times 1$) phase.

\[ \text{[1]} \text{ S. Jobic, P. Deniard, R. Brec, J. Rouxel, A. Jouanneaux, and A. N. Fitch, Zeitschrift für anorganische und allgemeine Chemie 598, 199 (1991).} \]
\[ \text{[2]} \text{ G. L. Pascut, T. Birol, M. J. Gutmann, J. J. Yang, S.-W. Cheong, K. Haule, and V. Kiryukhin, Phys. Rev. B 90, 195122 (2014).} \]
\[ \text{[3]} \text{ P.-J. Hsu, T. Mauerer, M. Vogt, J. J. Yang, Y. S. Oh, S.-W. Cheong, M. Bode, and W. Wu, Phys. Rev. Lett. 111, 266401 (2013).} \]