Experimental Discovery of a Correlated Oxide Topological Insulator

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Topology has introduced a new paradigm in solid state physics¹-³. Materials with non-trivial, symmetry-protected topological order form the class of topological insulators, exhibiting robust conductivity at the surface while remaining insulating within the bulk¹-³. After the first experimental hallmark was set in 2007 by the confirmation of 2D topologically insulating behavior for HgTe/CdTe-heterostructures⁴, a variety of topologically non-trivial materials was found using optical conductivity and angle-resolved photoemission spectroscopy investigations⁵. The entry of scanning probe microscopy and spectroscopy added further insight regarding the expansion and localization of the related conducing surface states, promoting the pursuit of technological applicability of topological phenomena⁶-⁸. However, up to now all confirmed topological insulators are either metallic alloys⁹ with small band gaps or exhibit small domain sizes⁸ and therefore have limited use for real life applications. Here, we present experimental results on the surface of the transition metal oxide Na₂IrO₃, bridging the fields of topology and strongly correlated materials. Standard description of the electronic structure of Na₂IrO₃ fails, since spin–orbit coupling, bandwidth, on-site Coulomb repulsion and Hund's coupling are all equally important and typical approximations are invalid⁹,¹⁰.

On the one hand, we report on a scanning tunneling spectroscopy study revealing a V-shaped density of states within a bulk band gap comparable to silicon at 300 K. On the other hand, we discuss the up to now not considered general issue of addressability of topologically protected surface states. It offers a natural explanation for the discrepancies in former experimental results regarding this material¹⁰-¹³, providing a coherent picture of topologically protected and trivial conductivity channels in Na₂IrO₃.

Correlated transition metal oxides constitute a promising new class of large band gap topological materials. Avoiding the chemical instability of Na₂IrO₃ at ambient atmosphere by suitable coating opens up the perspective to realistic technological operability of this 3D topological insulator.

Correlated honeycomb transition metal oxides (TMO’s) A₂IrO₃ (A= Li, Na) do not only attract large attention for realizing the magnetic Kitaev exchange interaction¹⁴-¹⁹ but also for being predicted by theory to be topologically insulating²⁰-²³. This is remarkable, as spin-orbit coupling is not the solely dominating factor regarding the formation of the bulk band gap. Crystal-electric field splitting and Coulomb correlations contribute at comparable energy scales⁹,¹⁰,¹⁴-²¹,²³-²⁵, with the latter being indispensable to explain the existing band gap¹⁰. The layered crystal structure of Na₂IrO₃ is depicted in figures 1a-c. Experimentally, macroscopic methods provide a diffuse picture, even regarding the band structure of Na₂IrO₃. On the one hand, band gaps between 340 meV and 1 eV were found by using optical conductivity and angle-resolved photoemission spectroscopy (ARPES)¹⁰,¹³. On the other hand, metallic surface states were observed in further ARPES measurements¹¹. Scanning tunneling microscopy (STM) experiments on freshly cleaved Na₂IrO₃ crystals revealed two different surface reconstructions, associated to the Na₃[(1x1)]- and NaIr₂O₆[(\sqrt{3}x\sqrt{3})R30°] termination. Band gaps of 1.2 eV and 0.6 eV were observed respectively¹².

In this work, we propose a model which potentially resolves these contradictions. We have observed the access to different conductivity channels in dependence of surface and tip modifications, allowing us to identify hallmarks of 3D topological
insulator behavior inside the robust bulk band gap. We execute this by using a home-built STM/STS setup on freshly cleaved crystals in UHV at room temperature. Details are found in the methods section.

In constant current topography, the known (1x1) and (√3x√3)R30° terminations as well as a third surface structure showing up as a stripy pattern superimposed on the regular (1x1)-reconstruction was found (see extended data figure 1). Spectroscopically, this stripy reconstruction is indistinguishable to the (1x1)-reconstruction. As our findings on topologically protected states are similar for the (√3x√3)R30° surface, we focus on the (1x1)-reconstruction.

dl/dV-spectra recorded on the (1x1) reconstructed surface are depicted in figure 1f. At clean surfaces a band gap of 0.8 eV is visible in accordance with previous STM investigations12. We will refer to this gap between the valence band edge at -0.45 eV and the conduction band edge at 0.35 eV as the bulk band gap. However, spectra taken at defects paint a very different picture: the band gap is entirely closed in a V-shaped fashion. This is the expected spectroscopic signature for a gapped band structure with a gap closing via a Dirac-cone, as illustrated in figures 1d and 1e, i.e. the signature of a topologically protected conducting channel. First deviations from this V-shape are found at the onset of tunneling into the valence and conduction bulk band states.

Two questions arise: firstly, why is the supposed TI-state not always apparent, as its predicted robustness should force it to be2. And secondly, what influence have defects on the observable conducting channels.
In the following we show, that the key to understand these issues is the addressability of different electronic states, i.e. whether at each surface point existent states can be observed experimentally or not.

\( \text{Na}_2\text{IrO}_3 \) exhibits a high density and variety of defects, ranging from single vacancies to ridge-like defects and massive cracks (see extended data figure 2). Sodium within the surface-layer shows a high mobility, causing Na-modifications of the STM-tip apex by chance. We used this circumstance to get access to differing tunneling channels. Attachments and detachments of sodium cause corresponding modifications of the tip length, resulting in vertical jumps in the topographic data. Simultaneous topographic and spectroscopic measurements link changes in tip modifications to observable spectroscopic features.

Topologically protected conductivity is categorized by dimensionality, resulting in 1D conducting channels at step edges for 2D topological insulators and 2D conducting surfaces for 3D topological insulators\(^1\)\(^-\)\(^3\). Consequently, the inclusion of step edges into the investigation is highly recommended.

An STM/STS-dataset covering three single step edges as well as a tip modification is depicted in figure 2. All terraces exhibit a (1x1)-reconstruction. Marked by a black arrow, the topography displays a drop in the topographic height by 0.43 nm, reflecting the tip modification. Since the fast scan axis is oriented from top to bottom, we propose that tip-attached sodium was disposed in the process. For further discussion, we divide the probed area into two regions: region I covers the area examined before and region II the area after the tip modification. Atomic resolution was maintained for both regions (see extended data figure 3). Snapshots of spectroscopy maps at -1.0 V, -0.5 V, 0.0 V, 0.5 V and 1.0 V exhibit the significant impact on the measurable spectra due to the tip modification (figure 2c).

All spectra in figures 2a and b show a closed band gap, independently of the electronic properties of the STM-tip or the local surface structure. The gap closing is always V-shaped with the respective minimum being located at the Fermi-level, as can be seen in the zoom-in depicted in figure 2b. However, the absolute conductivity varies significantly on a
local scale. This can be attributed to the addressability of these states.

In region I, the dI/dV-spectra show additional broad peaks at -0.5 V and 0.5 V (figure 2a, green curves) when measured on terraces. We attribute these peaks in the dI/dV curves to defect conductivity. The huge density and variety of the defects broadens the corresponding energy interval, resulting in defect bands. The defect peaks disappear at or nearby step edges (figure 2a, blue curves). For this alternative finding compared to figure 1f, the tip configuration is the only possible cause, as termination and defect structure are identical. The fact that the conductivity at step edges does not disappear entirely close to the fermi level even though the defect peaks vanish is a first hint that it is not defect conductivity that closes the band gap. Comparing regions I and II, i.e. different tip modifications, provides further insight.

Although the shape of all measured dI/dV-curves drastically changes in region II compared to region I, the V-shape at the Fermi level persists. All spectra taken at terraces in region II resemble the red spectra in figure 1f qualitatively. However, the overall conductivity provided is different on the three terraces. At the topographically highest and lowest terraces (figure 2a, yellow curves), this conductivity is substantially lower than at the terrace in between (figure 2a, red curve). Across step edges, the spectra smoothly change in regards of conductivity without transforming to a different overall shape (see extended data figure 4). The combination of V-shaped band gap closing and persistence across step edges indicates the existence of protected surface conductivity with Na$_2$IrO$_3$ being a 3D topological insulator.

We deduce from all these observations that even though different conducting channels like topologically protected surface states, defect bands and the bulk bands are always present (for V-shaped band gap closing at the (\sqrt{3}x\sqrt{3})R30° reconstruction see extended data figure 5), the interplay of electronic structure of tip and surface determines if and to which extend these channels are addressable by the tunneling process.

Assuming that the here found defect structure is common for Na$_2$IrO$_3$ surfaces, non-STM investigations$^{10,11,13}$ may have underestimated the band gap due to the existence of defect bands. In the case of the reported laterally resolved STM/STS experiments$^{12}$, addressability issues have been overlooked, missing out the variety of phenomena presented in this letter.

Finally, we briefly discuss alternative explanations of our experimental findings. Triggered by the high defect density on the surface, defect induced conductivity as underlying phenomenon cannot entirely be ruled out. However, a linear dI/dV is not associated with such defect conductivity. The interpretation of the minimum at the Fermi energy as the signature of a Coulomb gap seems very unlikely with a gap size of several hundred mV for a 2D system at 300 K. This leaves room for some form of exotic surface state as an alternative model compared to topologically protected surface conductivity. As Na$_2$IrO$_3$ represents a class of materials that lies at the intersection of topology, correlated-electron systems and surface physics, a comprehensive theoretical description has to be developed. The honeycomb iridates can serve as prototypical sample-systems to accompany this experimentally.

In summary, we report the first experimental evidence of a TMO to be topologically insulating with a bulk band gap of 0.8 eV, comparable to common semiconductors. The combination of electronic properties of the STM-tip as well as the local surface structure has a severe impact on the dI/dV-spectra, bringing addressability of the TI-state into the focus. Three basic accessible conducting channels are identified: regular bulk conductance for voltages greater than the bulk band gap, conductance via defect bands and finally topologically protected surface conductance. Future investigations of the addressability of electronic states are key for the disentanglement and experimental identification of topological properties.

In general, a topological insulator with a bulk band gap of 0.8 eV is a substantial leap towards the technological use of protected surface states, resulting in the prospect of 2D electronics with monatomic thickness. Obviously, the suppression of defects and therefore the defect bands is crucial on
the path to make 3D topological insulators like Na$_2$IrO$_3$ technologically applicable.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (DFG) for financial support via Projects 220179758 (SPP 1666) and 107745057 (TRR 80).

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Methods

Measurements were performed in a homebuilt ultrahigh vacuum (UHV) scanning tunneling microscope (STM) at pressures below $5 \times 10^{-10}$ mbar at 300 K. Single crystalline Na$_2$IrO$_3$ was grown using solid-state synthesis, resulting in thin plate shaped crystals with a diameter up to 4 mm. Polycrystalline material was grown and characterized as described in former works$^{26,27}$. After adding 10% extra Ir powder, the mixture was heated up to 900°C, cooled and ground. Afterwards, the product was heated to 1050°C. This results in small single crystals. Larger crystals were obtained by an additional annealing with slow heating to 1050°C followed by a long hold time. Magnetic susceptibility measurements revealed a sharp signature at $T_N$, confirming good crystalline quality. To achieve clean surfaces, the crystals were cleaved in UHV and directly transferred to the STM probing stage. STM topography images were acquired using constant current mode. All voltages refer to the sample bias voltage with respect to the tip, all currents refer to the tunneling current between tip and sample. To gain full scanning tunneling spectroscopy (STS) maps $dI/dV$-spectra were recorded at every second pixel in the topography using lock-in techniques for enhanced resolution. Additionally $I/U$-curves were recorded without lock-in techniques and used for the calibration of the $dI/dV$-curves. The absolute calibration error can be estimated to <0.5 pA/V at free surfaces and <2.6 pA/V at step edges.

The used tungsten STM-tips were prepared by electrochemical etching in a KOH-solution, and further processed by annealing and argon sputtering in UHV. In-situ modifications by Na occur by chance due to the high sodium mobility on the Na$_2$IrO$_3$ surface. Intentional cleaning of the tip is done by applying voltage pulses up to 5 V.

Acquired data was analyzed and visualized using the home build software NextDiagram ver. 5.2.1. Visualization of the Na$_2$IrO$_3$ crystal structure was done using VESTA ver. 3.2.1.

Data availability

The scanning tunneling microscopy and spectroscopy data sets provided in this work, as well as additional crystal characterization data are available from the authors.

Code availability

Code used in this work is available from the authors on request.

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Contributions

M.W., P. G. and T.D. planned the experiments. T.D., M.W. and G.T. set up the technical requirements for the experiment. I.P. and P.G. provided the samples and executed their preliminary characterization. T.D. carried out the experiments. T.D. and M. W. performed the data analysis. T. D., P.G. and M.W. wrote the manuscript; all authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing financial interests.
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Extended Data

Figure 1 | Stripy pattern superimposed on the (1x1)-reconstruction. a, 50 nm x 50 nm constant current topographic map covering four (1x1)-terraces, recorded using a setpoint of -1.5 V and 100 pA. A superimposed stripy rearrangement of the sodium atoms at the surface is visible. These structures do not extend over surface defects or step edges. Spectroscopically, no difference compared to the regular (1x1)-reconstructed surface is measurable b, zoom-in on the stripy pattern in a. Every stripe consists of two rows of sodium atoms. The distance between the stripes varies without long range periodicity.
Figure 2 | High defect density observed on Na$_2$IrO$_3$ surfaces. a, 100 nm x 100 nm constant current topographic map showing various defect structures on the (1x1)-reconstructed Na$_2$IrO$_3$ surface, recorded using a setpoint of -1.5 V and 100 pA. The dashed red boxes mark the positions of the zoom-ins depicted in b-e. b, ridge-like defect with a topographic height of approximately 100 pm. c, “stripy” pattern superimposed to the regular (1x1)-reconstructed surface, bordered by various defects. The pattern does not extend over any defects. d, crack in the topmost crystal layer (here: Na$_3$ layer). Such cracks extend over several hundred nanometer and locally exhibit small sodium aggregations. e, different surface defects, ranging from vacancies due to missing single sodium atoms to large defect aggregations.
Figure 3 | Maintaining atomic resolution despite tip modifications. a, constant current topography of the (1x1)-reconstructed surface, recorded using a setpoint of -1.5 V and 100 pA. Two consecutive tip modifications occur in the center of the topography, indicated by abrupt jumps of the topographic height. b, same topography as in a with adjusted height to smoothen the topographic jumps caused by the tip modifications. c, average dI/dV spectrum before the tip-modification. d, average dI/dV spectrum after the tip-modification.
Figure 4 | Impact of step edges on the topologically protected state. a, dl/dV-spectra recorded equidistantly across a single step edge. The surface is (1x1)-reconstructed at on both terraces. The lateral distance between the spectra is 1 nm. The actual recording positions are marked in the inset and color coded according to the dl/dV-curves. A smooth transition of the curves is observed when crossing the step edge, without any change in the qualitative shape of the spectra. However, the overall conductivity is altered. The deviation regarding the valence band onset at bias voltages lower than -0.8 V is due to the fact that the integral of the dl/dV-curves from the setpoint to the fermi-level has to be constant. b, Zoom-in according to the grey dashed box in a. The band gap closing is always V-shaped, resembling a protected state of a 3D topological insulator.
Figure 5 | Simultaneous observation of an open band gap as well as a V-shaped band gap closing for the \((\sqrt{3} \times \sqrt{3})R30^\circ\)-reconstructed surface. a, constant current topographic map covering one (1x1)-terrace and two \((\sqrt{3} \times \sqrt{3})R30^\circ\)-terraces, recorded using a setpoint of -1.5 V and 100 pA. b-d, dl/dV-curves taken at the terraces corresponding to the marking with blue arrows.