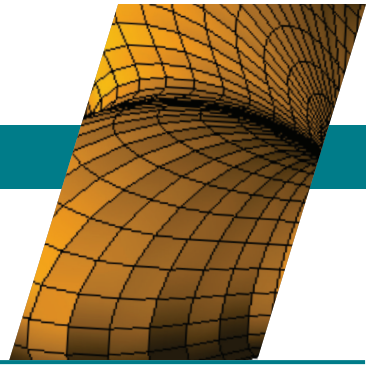
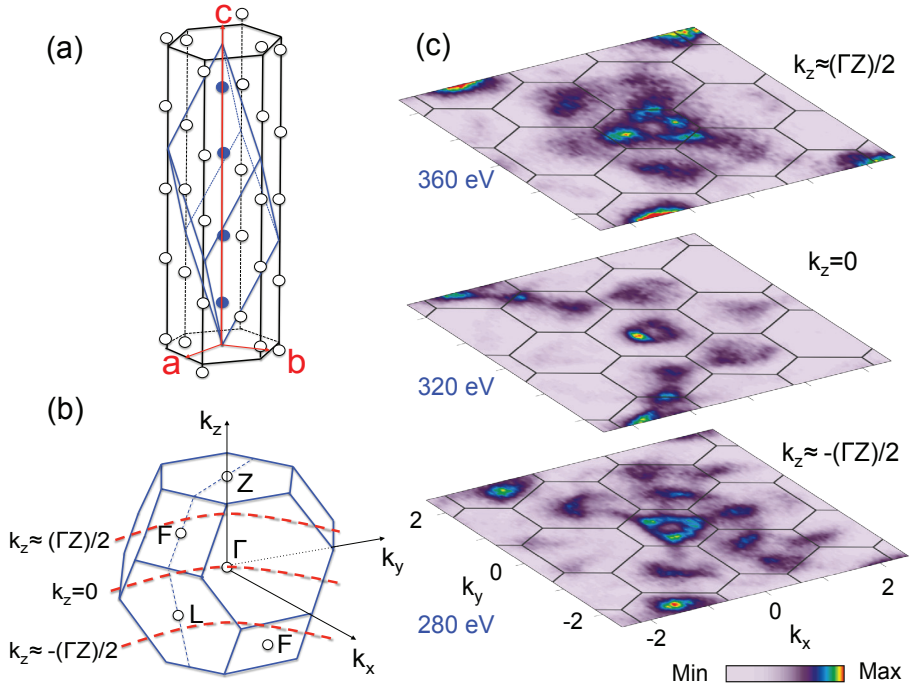


ARPES Overturns V_2O_3 Metal-to-Insulator Theory



(a) V_2O_3 crystal structure showing the hexagonal unit cell (black lines) and the primitive rhombohedral cell (blue lines), with four vanadium atoms (blue circles) in the center. (b) Brillouin zone for the metallic-phase rhombohedral unit cell. (c) Wide angle-dependent slices of the Fermi surface of V_2O_3 (as indicated by dashed red lines in b) at T = 200 K (metallic phase). A triangular-shaped feature reverses direction above and below the Brillouin zone center.

Science In Progress

The metal-to-insulator transition in V_2O_3 (vanadium sesquioxide) has a long history of explanatory models being proposed, generally accepted, and overturned by new experiments. Ever since reports revealing the full doping-pressure-temperature phase diagram for V_2O_3 were published in 1969–1973, successive generations of condensed-matter physicists have been determined to solve the mystery of why V_2O_3 behaves the way it does. One reason for this was that it seemed to be the perfect examplar of a type of insulator proposed by Nevill Mott in 1949. A "Mott insulator" is a material that's expected to be a conductor, but isn't, despite having a half-filled outer electron orbital (a characteristic of metals). The repulsion between the electrons in this orbital causes them to localize, creating an energy gap between filled localized states (where the electrons are immobile) and a conduction band (where they can move around). Subsequent models incorporated more complexity, but remained unconfirmed by empirical data. In this work, Lo Vecchio et al. provide such data—an important check on a decade-old picture, suggesting that there is still more work to do.

Materials that can both conduct and insulate against the flow of electricity are of great interest for use as components in advanced electronic devices as well as for fundamental condensed-matter studies. Nearly 50 years ago, the transition-metal oxide V_2O_3 was found to qualify as such a material, being a conductor (i.e., metallic) above 160 K and an insulator below. Despite progress in methods to model these observations theoretically, the lack of momentum-resolved photoemission data to verify the theories meant that the origins of this phenomenon ultimately remained a mystery. Now, researchers report on angle-resolved photoemission spectroscopy (ARPES) measurements performed on samples of V_2O_3. The results overturn a decade-old theory about metal–insulator transitions (MITs) in this material and provide a spectroscopic benchmark test for future models.

Initially, V_2O_3 was thought to be a real-world example of an ideal Mott MIT, in which the insulator state arises as a result of Coulomb repulsion between electrons. However, this was quickly challenged on the grounds that it didn't take into account the material's multi-orbital electronic structure: each trivalent vanadium ion has two 3*d* electrons distributed between two overlapping d-orbitals (a_{1g} and e_g^{π}).

In the late 1990s, the integration of density functional theory (DFT) with dynamical mean-field theory (DMFT) gave real hope of solving the mystery within a realistic multiorbital calculation. Bulk-sensitive angle-integrated photoemission provided a basic confirmation of the DMFT theory, but was not able to discriminate between the details of different DFT+DMFT theories.

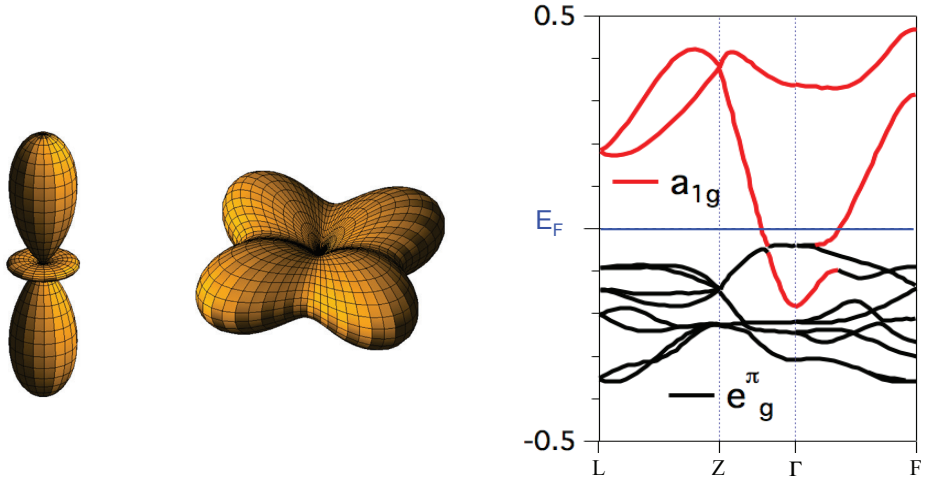
A series of DFT+DMFT studies in the early 2000s coalesced in 2007 around a particular model in which Coulomb

repulsion forces drive the splitting of the a_{1g} and e_g^π states in the metallic phase to the brink of an insulating gap near the MIT. Small structural perturbations from temperature changes and doping would then be needed to push the system over the transition. The model's predictions included a Fermi surface featuring a single a_{1g} electron pocket, as well as completely filled e_g^π bands. Over time, however, technical advances in the DFT+DMFT calculations began to show discrepancies with the 2007 model, setting the stage for the next logical development: measurement of the momentum-resolved band structure of V_2O_3.

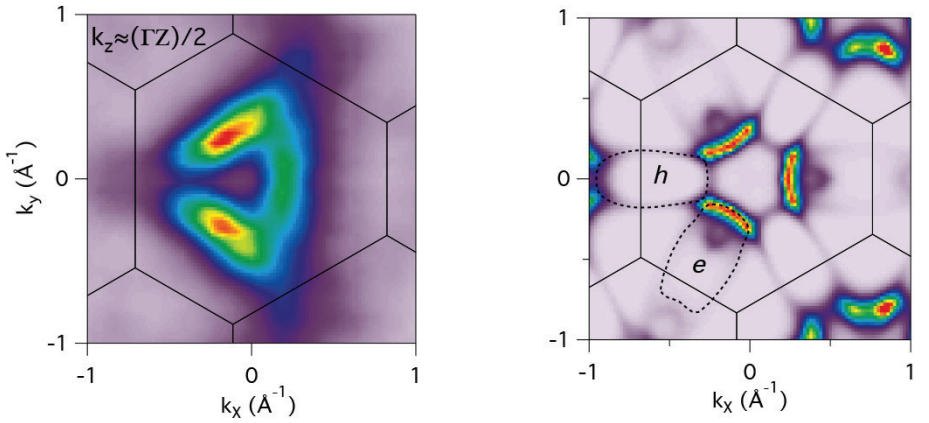
Scientists at the ALS performed ARPES experiments on single-crystal V_2O_3 samples using the 2009 configuration of Beamline 7.0.1 (the ARPES program has since moved to Beamline 4.0.3). The wide-angle detection capability of the beamline's electron spectrometers was important for characterizing the weak-contrast, angle-dependent, band-structure changes in the rather broad features inherent in the V_2O_3 spectra. The measurements were taken at a temperature of 200 K, fully in the metallic phase.

The measurement of a triangular Fermi surface with a hole-like band dispersion—as opposed to an electron pocket—was the crucial observation directly contradicting the 2007 theory. While the key Fermi surface and band dispersion data were acquired at a photon energy of 180 eV, the wide photon-energy range of Beamline 7.0.1 (80–900 eV) also allowed the verification of the triangular Fermi surface feature at more bulk-sensitive ranges, thus helping to prove the bulk origin of features that were measured at lower, more surface-sensitive, energies.

To support their findings and gain greater insight, the researchers performed band calculations using DFT+*U* methods (*U* is a parameter accounting for the Coulomb repulsion between electrons). A match was found for the specific half-filling of the e_g^π band observed in the data. The calculations also gave rise to a Fermi-surface contour with an open-tipped triangular feature very similar in size and shape to that obtained via the ARPES experiments. In the future, analysis using the more-sophisticated DMFT will be needed to fully explain the details of the experimental data and to provide a new explanatory mechanism for the metal–insulator transition in V_2O_3.



The a_{1g} (left) and e_g^π (center) molecular orbitals of V_2O_3, represented graphically in 3D and in band-structure ("spaghetti") plots (right).



Comparison of the triangular Fermi-surface feature obtained from ARPES data (left) and from DFT+*U* calculations (right).

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