

Itinerant-to-Localized Transmutation of Electrons Across the Metal-to-Insulator Transition in V_2O_3

The most familiar physical property of materials is their ability to conduct (metals) or not conduct (insulators) electric current. The conductivity of metals increases when the temperature decreases. Thus, copper conducts current ten times better at -200°C than at 400°C . But for V_2O_3 , a metal at room temperature, the conductivity drops sharply by a factor of a million when the temperature falls below -113°C , becoming a so-called Mott insulator. How to explain this astonishing transition? We revealed for the first time how the itinerant, wave-like electrons in the metallic phase of V_2O_3 localize across the Mott metal-insulator transition.

The metal-to-insulator transition is a major mystery because, according to the conventional quantum model describing electrons in solids (Bloch's theory), the metallic or insulating character of a material depends only on its number of electrons. According to this model, electrons progressively fill states in regions of allowed energies (called energy bands) separated by regions of forbidden energies (gaps). If the last occupied energy band is partially filled, the material is metallic and the electrons are mobile. If it is completely filled, the material is insulating [1]. Since the number of electrons in a material does not change with temperature, a metal, according to Bloch, must remain a metal as it is cooled down.

What happens in V_2O_3 that violates this well-tested model? The last partially occupied band is formed from orbitals strongly localized in space—the vanadium $3d$ orbitals. The electrons cannot easily avoid each other and are subject to strong mutual repulsion, which is neglected in Bloch's model: the electronic correlations. At low temperatures, this repulsion prevents the elec-

trons from moving, making the compound an insulator [2, 3], as shown in Fig. 1. Even more mysteriously, the electronic transition is accompanied by both an antiferromagnetic and a structural phase transition [2-4].

The metal-insulator transition is thus a manifestation of electronic correlations, but the microscopic processes accompanying it remain controversial despite 50 years of research. The evolution of the electronic energy bands during the transition had not been observed. Although such observation could be performed by angle-resolved photoemission spectroscopy (ARPES), it had not been done so far for several important technical reasons, one being that single crystals break into pieces due to the brutal structural change across the transition. In new experiments [5] carried out in part at beamline 2A, these problems were circumvented by working on a thin film of V_2O_3 deposited on a sapphire substrate. The substrate acts as an "anchor" that prevents the material from breaking when cooled down through the transition.

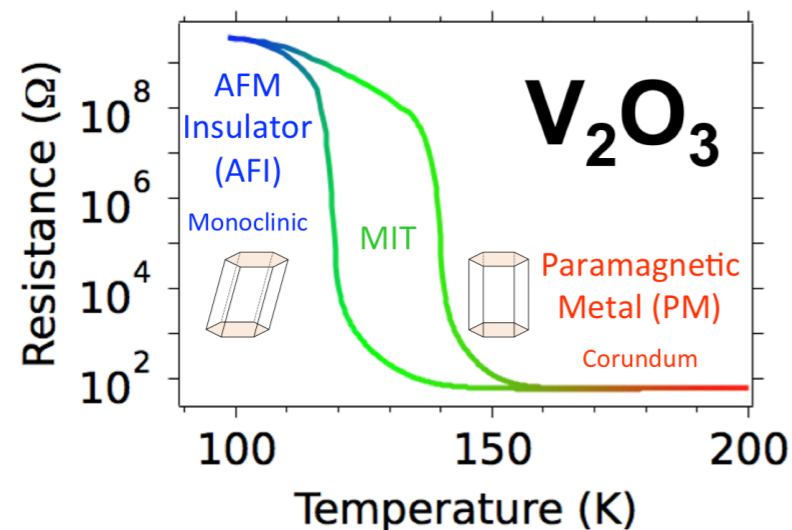


Figure 1: Electrical resistance (showing a hysteresis cycle) measured on a V_2O_3 film used in this work. The conventional cells in the metallic and insulating phases are also depicted.

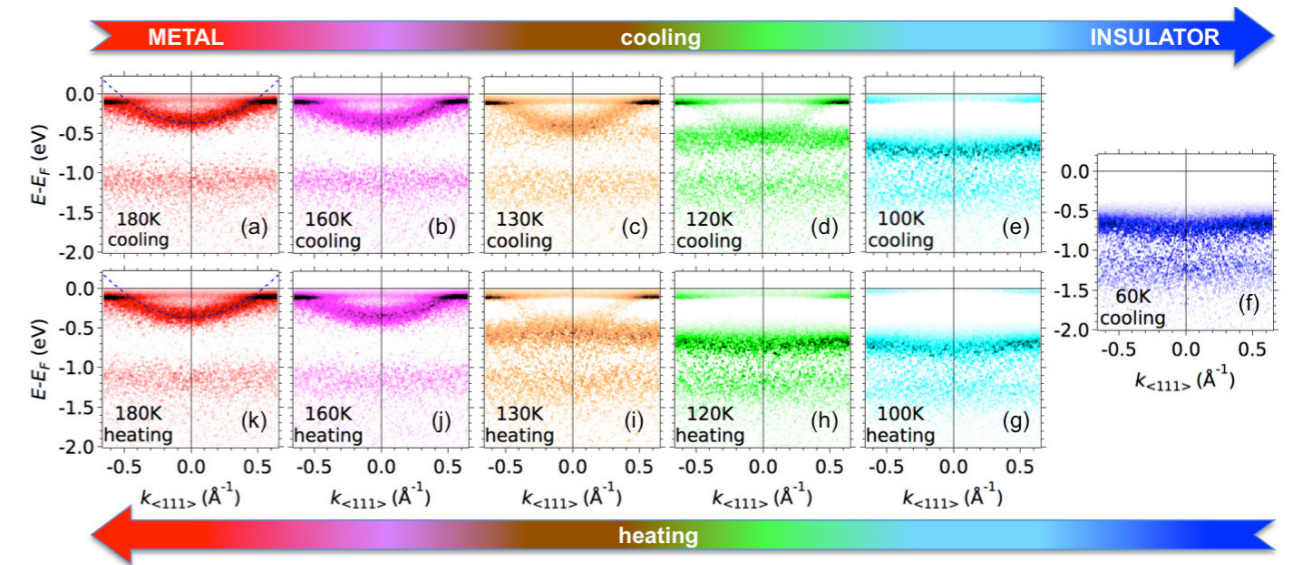


Figure 2: Evolution of the electronic structure of V_2O_3 measured by ARPES as a function of temperature through its metal-insulator transition, as the temperature is decreased (panels (a) to (f)), or increased (panels (f) to (k)).

The main result of this study [5] is presented in Fig. 2. The figure shows the evolution of the energy bands measured by ARPES during the metal-insulator transition when the temperature is decreased (panels (a) to (f)), or increased (panels (f) to (k)). The measurements clearly show the transition:

- At 180K (i.e. -93°C , red image), a parabolic-shaped energy band (typical of mobile free electrons) intersects the Fermi energy (set to zero): the compound is metallic.
- At 60K (-213°C , dark blue image), there are no more electronic states in this energy zone: V_2O_3 has become insulating.

When the temperature drops to a value between 180K and 60K, the intensity of the parabolic band decreases gradually, while a horizontal band, typical of electrons remaining localized on the atomic sites, becomes more and more intense, indicating that mobile electrons "transmute" into localized electrons. Moreover, this horizontal band moves gradually towards higher binding energies. The trend is reversed by heating, but with a shift in temperature (compare the images at 120K and 130K by cooling and heating cycles), which can be explained by the formation, at intermediate temperatures, of metallic and insulating islands whose proportion depends on the previous state of the material.

This first imaging of the evolution of the electronic structure of V_2O_3 during its transition from metal to insulator reveals that it occurs as a gradual transfer of itinerant electron states to localized states. It shows that the

metal-to-insulator transition involves a complete reorganization of several energy bands.

REFERENCES

- [1] N. W. Ashcroft and N. Mermin, in *Solid State Physics* (Brooks/Cole, 1976).
- [2] N. F. Mott, *Mod. Phys.* **40**, 677 (1968).
- [3] D. B. McWhan, T. M. Rice and J. P. Remeika, *Phys. Rev. Lett.* **23**, 1384 (1969).
- [4] R. M. Moon, *Rev. Lett.* **25**, 527 (1970).
- [5] M. Thees, M.-H. Lee, R. L. Bouwmeester, P. Rezende-Gonçalves, E. David, A. Zimmers, F. Fortuna, E. Frantzeskakis, N. Vargas, Y. Kalcheim, P. Le Fèvre, K. Horiba, H. Kumigashira, S. Biermann, J. Trastoy, M. Rozenberg, I. Schuller and A. Santander-Syro, *Science Advances* **7**, eabj1164 (2021).

BEAMLINE

BL-2A

M. Thees¹, M.-H. Lee², R. L. Bouwmeester³, P. H. Rezende-Gonçalves^{1,4}, E. David¹, A. Zimmers⁵, F. Fortuna¹, E. Frantzeskakis¹, N. M. Vargas², Y. Kalcheim^{2,6}, P. Le Fèvre⁷, K. Horiba⁸, H. Kumigashira^{8,9}, S. Biermann^{10,11,12}, J. Trastoy¹, M. J. Rozenberg¹, I. K. Schuller², A. F. Santander-Syro¹ (¹Univ. Paris-Saclay, ²Univ. of California, ³Univ. of Twente, ⁴Univ. Federal de Minas Gerais, ⁵Sorbonne Univ., ⁶Technion, ⁷Synchrotron SOLEIL, ⁸KEK-IMSS-PF, ⁹Tohoku Univ., ¹⁰Institut Polytechnique de Paris, ¹¹Collège de France, ¹²Lund Univ.)