The physics of ultra-thin vanadium dioxide: At the surface, interface, and in-between

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Most common materials can be characterized as either a good conductor of electricity, like a copper wire, or a poor conductor, like the rubber insulation on that wire. Now, imagine a single material that can actually switch between these two states. Although rare, such materials that exhibit a so-called metal-to-insulator transition do exist and they could be extremely useful in the next generation of electronic devices.

Metal-to-insulator transitions are generally found in a class of compounds known as “strongly correlated” materials. These are materials whose electrons do not flow independently, as they do in traditional metals, but rather their behavior is linked or correlated with one another. This electron correlation can give rise to a wide range of exciting phase transitions that can be triggered by many different things, such as temperature, pressure, or simply shining light on the special material, making them suitable for many types of switches and sensors. For example, this is the same class of materials where in some cases superconductivity can be found at very low temperatures.

Vanadium dioxide (VO$_2$) is one particularly interesting strongly correlated material that exhibits a reversible metal-to-insulator transition that is nearly instantaneous and can be triggered by warming it only slightly above room temperature. This makes it a strong candidate for use in future technology in our every-day lives. There are already many different proof-of-concept devices that utilize the metal-to-insulator transition of VO$_2$. Specific applications include next generation data storage, computer transistors that are only a fraction of the size of current technology, and even “smart” window coatings, which could either filter or transmit heat to passively control indoor temperature. However, to really bring these and many other new
technologies into fruition requires a deep understanding of the physics behind this metal-to-insulator transition, such that we can manipulate it and fine-tune it for a specific purpose.

Not all metal-to-insulator transitions are the same. In some materials, a metal-to-insulator transition occurs because of electrons interactions with other electrons. In others, it is caused by the electrons interacting with the atoms themselves, referred to as the lattice. The metal-to-insulator transition of VO₂ is a peculiar case because there is strong experimental evidence that both of these interactions are prevalent during the transition. This has led to a debate in the scientific community since its initial discovery in 1959: is it electron-electron interactions, electron-lattice interactions, or some combination of the two that are responsible for this metal-to-insulator transition?

In this dissertation, this metal-to-insulator transition was studied by subjecting VO₂ to varying amounts of strain. By looking at how the material responds to strain, we can gain insight into the root cause of the transition. Here, this is achieved by putting a very thin layer of VO₂ on top of a similar material, titanium dioxide (TiO₂). Since VO₂ is naturally smaller than TiO₂, when grown this way it is forced to stretch itself such that each of its atoms lines up with the atoms from the TiO₂ substrate. This only works when the VO₂ layer is a few dozen atoms or less in thickness. This method can stabilize a very large stress on the material that would normally shatter a stand-alone piece of VO₂. Growing VO₂ in this way, is a challenge in itself, so we collaborated with a group of researchers at Cornell who have the necessary expertise.

To investigate the electronic properties of this ultra-thin strained VO₂, we used x-ray spectroscopy. This is an experiment that often requires travelling to a synchrotron – a building-sized machine that produces extremely bright x-rays (typically 10 billion times brighter than the sun!). It can be thought of as a giant microscope that can be used to observe the electrons within a
material. Specifically, we employed two types of x-ray spectroscopy: hard x-ray photoelectron spectroscopy (HAXPES) and x-ray absorption spectroscopy (XAS). The combination of these two x-ray techniques allowed us to see into the material and understand how the electrons interact with their surroundings.

In the case of these extremely thin layers of VO₂, these experiments are not straightforward. Often, materials have different properties at their top surface or in the bottom interface, the region where it makes contact with another material. The difficulty in distinguishing these regions from the “in-between” region of genuine VO₂ in such a thin layer, has really hindered progress on this issue for the past two decades. To overcome this and to make sure we would be able to hone in on the desired region, we designed a study comparing VO₂ films of varying thickness. This early work, published in the journal *Materials*, demonstrated our experimental approach and data analysis techniques used to study ultra-thin VO₂ and how they can be applied to other materials with phase changing behavior.

Once our methodology was in place to distinguish these regions, indeed it was discovered that the electronic properties of both the surface and interface regions are drastically different from that of ordinary VO₂ in the center. At the surface of VO₂, the very last vanadium atom has less oxygen atoms surrounding it. This changes how the atoms bond together and does not allow for a metal-to-insulator transition in these atoms. On the other end, the interface, due to the chemical similarities between VO₂ and the underlying TiO₂, the titanium atoms can frequently mix into the VO₂ film resulting in an entirely different material in this region. This mixed material also does not allow for a metal-to-insulator transition.

Excluding these regions, focusing our studies only on the film interior, it was not yet clear that the extremely small thickness required for creating strain, would not in itself alter the metal-
to-insulator transition. In many materials, scaling to such small dimensions can often dramatically change their electronic properties. However, in the case of VO₂, we found that a metal-to-insulator transition can still occur in thin VO₂ films only a few atoms (a single nanometer) in thickness. In this ultra-thin VO₂ we found that its electronic properties in both the insulating and metallic state are indistinguishable from larger VO₂ crystals. This work, published in the journal *Nano Letters*, laid the ground work for studying the effects of strain.

Variation of the strain was achieved by choosing different surfaces of the TiO₂ substrate that stretch VO₂ films along different directions. By comparing differently strained VO₂ films, through our x-ray techniques, we were able to establish a link between strain and the resultant electronic properties. We found that straining along one particular direction can alter the preferred arrangement of electrons within the material. This rearrangement occurs in such a way that the electrons can interact with other electrons more freely. Because of this, the electron-electron interactions become enhanced relative to the electron-lattice interactions. This has a direct impact on the way that VO₂ can transition from the metallic state to the insulating state, and vice versa. These findings are published in an article and a subsequent Rapid Communication in the journal *Physical Review B*.

The results of this dissertation, have serious implications regarding the mechanism of this metal-to-insulator transition. The experiments revealed that both electron-electron and electron-lattice interactions are contributing causes to the metal-to-insulator transition. Furthermore, based on straining VO₂ and studying the modified electronic behavior, the delicate interplay between these two seemingly independent causes has been determined. This new understanding provides unprecedented predictive control over the metal-to-insulator transition of VO₂, paving the way for further innovation of new technologies.
THE METHOD – An ultra-thin film of VO$_2$ (purple) prefers to systematically line its atoms up with those of the TiO$_2$ substrate (blue), thus creating strain in the VO$_2$ film. This can be seen in an actual false-colored transmission electron microscope image (right), where a model of the atomic arrangement is overlaid. The scale bar represents 1 nanometer.

THE EXPERIMENT – Extremely bright x-rays from a synchrotron source illuminate the ultra-thin VO$_2$. This causes, both x-rays and electrons to be emitted, which are then detected in the XAS and HAXPES experiments.