

METAL-INSULATOR TRANSITIONS

Orbital control

On cooling, transition metal oxides often undergo a phase change from an electrically conducting to an insulating state. Now it is shown that the metal-insulator transition temperature of vanadium dioxide thin films can be controlled by applying strain.

Takashi Mizokawa

Compounds containing transition metal atoms usually make for exciting physics — and useful functionalities. Examples of phenomena where the presence of transition metals is an essential ingredient include photosynthesis (manganese), high-temperature superconductivity (copper), lithium-ion battery electrochemistry (cobalt and iron) and colossal magnetoresistance (manganese again). Most of these effects are directly or indirectly related to the degeneracy of the atomic d orbitals in the transition metal.

Many transition metal compounds come as oxides, and in some of them a metal-insulator transition takes place¹. Above a certain temperature, the material is electrically conducting (metallic phase), whereas below it is not (insulating phase): it's as though the electronic conductivity, one of the most fundamental physical properties of solids, is 'switched off'. These transitions are another instance in which d electrons — the Coulomb interactions between them and the degeneracy of their energy levels^{2,3} — play a significant role. And, writing in *Nature Physics*, Nagaphani Aetukuri and colleagues now show that the transition temperature of VO_2 , the archetypal metal-insulator transition system^{1,4}, can be tuned by exploiting the orbital configuration of the vanadium $3d$ energy levels⁵.

The V^{4+} ions in VO_2 each accommodate one electron in their $3d$ subshell. Because of the particular field symmetry at the locus of a V^{4+} ion — the nearest surrounding oxygen ions lie at the vertices of an octahedron — the energies of the five $3d$ orbitals have, for regular octahedra, only two distinct values. The triply degenerate t_{2g} orbitals (labelled x^2-y^2 , yz and zx) have a slightly lower energy than the doubly degenerate e_g (or σ^*) orbitals (labelled xy and $3z^2-r^2$). This type of energy-level splitting is known as octahedral ligand-field splitting and can be understood from point group theory.

As the VO_6 octahedra are non-regular — the equatorial and apical V–O bond lengths are different, resulting in a tetragonal

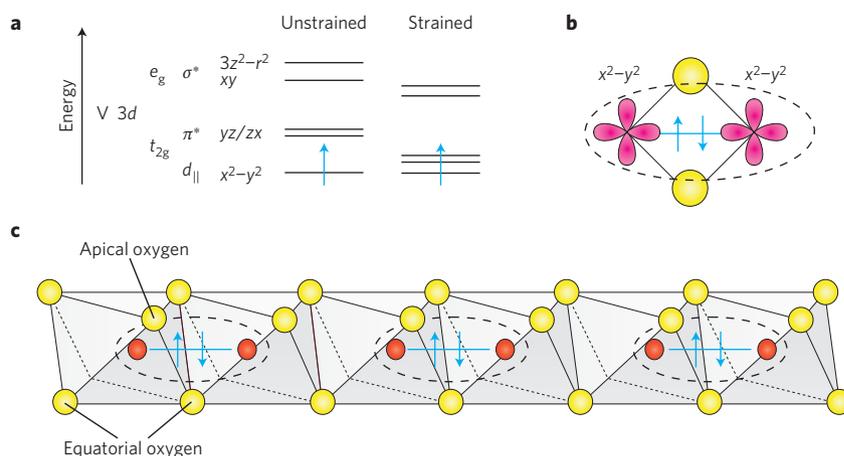


Figure 1 | Electronic states in VO_2 . Vanadium atoms are red and oxygen atoms yellow. **a**, The V $3d$ t_{2g} energy levels of the VO_6 octahedra are doubly degenerate (π^*) and non-degenerate ($d_{||}$). Initially, the V $3d$ electron occupies the $d_{||}$ level. In experiments performed by Aetukuri *et al.*⁵, strain-induced structural changes lead to shifted energy levels, with the π^* level lying significantly lower, closer to the $d_{||}$ level. **b**, Owing to the occupation of the x^2-y^2 orbitals, neighbouring V atoms dimerize and form 'bonds' with the two electrons occupying the same hybridized V–V x^2-y^2 orbital (shown in pink). **c**, Edge-sharing VO_6 octahedra in VO_2 with V–V dimers (encircled by dashed ovals) hosting one spin-up and one spin-down electron (blue arrows). The resulting charge-density wave induces an insulating state.

rather than a cubic structure — the t_{2g} orbitals are in turn split into two doubly degenerate π^* orbitals (yz and zx) and one $d_{||}$ orbital (x^2-y^2). It is the latter that has the lowest energy and therefore hosts the electron (Fig. 1a).

Along a certain direction, VO_6 octahedra with shared edges form a one-dimensional chain with the x^2-y^2 orbitals pointing to neighbouring vanadium ions (Fig. 1b). If the $3d$ electrons occupy these x^2-y^2 orbitals, a 1D electronic state along this chain can develop. Well-known metal-insulator transition mechanisms (for 1D systems) are the Peierls transition to a so-called charge-density-wave insulating state, where the V–V 'bond lengths' become alternatingly longer and shorter (dimerization)^{6,7} (Fig. 1c); and the Mott transition to a Mott insulating state, where the V $3d$ spins are basically localized at each V site and the neighbouring spins form a spin singlet⁸. Either way, the bottom line is that a structural change of

the VO_6 octahedra modifies local orbital symmetry of the V^{4+} ions, which can signify a symmetry breaking that results in a metal-insulator transition.

Aetukuri and colleagues now show that control of the orbital occupancy in VO_2 , and consequently control of the metal-insulator transition temperature, can be achieved for high-quality $\text{VO}_2/\text{RuO}_2/\text{TiO}_2$ substrate/buffer/thin-film structures⁵. The slight lattice mismatches between the three components of such heterostructures result in strained VO_2 thin films, and the degree of strain can be tuned by varying the thickness of the RuO_2 buffer layer. When the V–O apical bond length increases (due to the induced strain), the hybridization strength between the V $3d$ yz and zx orbitals and the O $2p$ orbitals (producing the V–O bond) reduces and the energy of the V $3d$ orbitals decreases (Fig. 1a). On the other hand, the hybridization strength between the V $3d$ x^2-y^2 orbital and the O $2p$ orbitals does

not change much because of the smaller change in the V–O equatorial bond length. Consequently, V 3*d* electrons can occupy the *yz* and *zx* orbitals rather than the x^2-y^2 orbital.

This simple ligand-field argument is nicely supported by the meticulous experiments performed by Aetukuri *et al.*⁵ using linear-dichroism soft-X-ray absorption spectroscopy. This technique enables the identification of the 3*d* electronic state (making use of the dipole selection rules for transitions from the 2*p* to the 3*d* levels), and has been successfully applied to studying interfaces of transition metal thin films⁹. The authors conclude that the occupancy of the 3*d* x^2-y^2 orbital is reduced by the elongation of the V–O apical bond, and that the electron–lattice coupling is therefore less strong, which results in a reduced transition temperature.

By combining state-of-the-art epitaxial thin-film growth with soft-X-ray absorption experiments at an advanced synchrotron radiation facility, Aetukuri *et al.* have taken an important step forwards in the development of future energy-efficient electronic devices: the VO₂/RuO₂/TiO₂ system with an orbitally controlled metal–insulator transition is indeed a strong candidate. However, as for the microscopic mechanism that induces this transition, it is not clear yet whether the electron–electron interaction contributes to the dimerization that results in the insulating state. Nevertheless, this study of VO₂ should spark further theoretical efforts to reveal the relationship between orbital symmetry breakings (Jahn–Teller effect, band Jahn–Teller effect and so on) and metal–insulator transitions (Peierls transition, Mott transition and others) in various transition metal compounds including VO₂ and Fe₃O₄.

Theoretical progress should then lead to precise predictions of feasible transition metal compounds for orbital manipulation. □

Takashi Mizokawa is in the Graduate School of Frontier Sciences, University of Tokyo, Chiba 277-8561, Japan.
e-mail: mizokawa@k.u-tokyo.ac.jp

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