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 place. 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, rather than a cubic structure — the $t_{2g}$ orbitals are in turn split into two doubly degenerate ($\pi^*$) orbitals (yz and zx) and one $d_{xy}$ 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$_2$ octahedra with shared edges form a one-dimensional chain with the $x^2−y^2$ orbitals pointing to neighboring 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)$^{12}$ (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 neighboring spins form a spin singlet$^4$. Either way, the bottom line is that a structural change of the VO$_2$ 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 VO$_2$/RuO$_2$/TiO$_2$ substrate/buffer/thin-film structures. 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 rather than a cubic structure — the $t_{2g}$ orbitals are in turn split into two doubly degenerate ($\pi^*$) orbitals (yz and zx) and one $d_{xy}$ orbital ($x^2−y^2$). It is the latter that has the lowest energy and therefore hosts the electron (Fig. 1a).

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not change much because of the smaller change in the V–O equatorial bond length. Consequently, V 3d 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 3d electronic state (making use of the dipole selection rules for transitions from the 2p to the 3d levels), and has been successfully applied to studying interfaces of transition metal thin films\(^9\). The authors conclude that the occupancy of the 3d $x^2-y^2$ 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 VO$_2$/RuO$_2$/TiO$_2$ 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 VO$_2$ 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 VO$_2$ and Fe$_3$O$_4$.

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

References

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