Mechanism of metal-to-insulator transition in ruthenium phosphide suggests a new way of looking at solids

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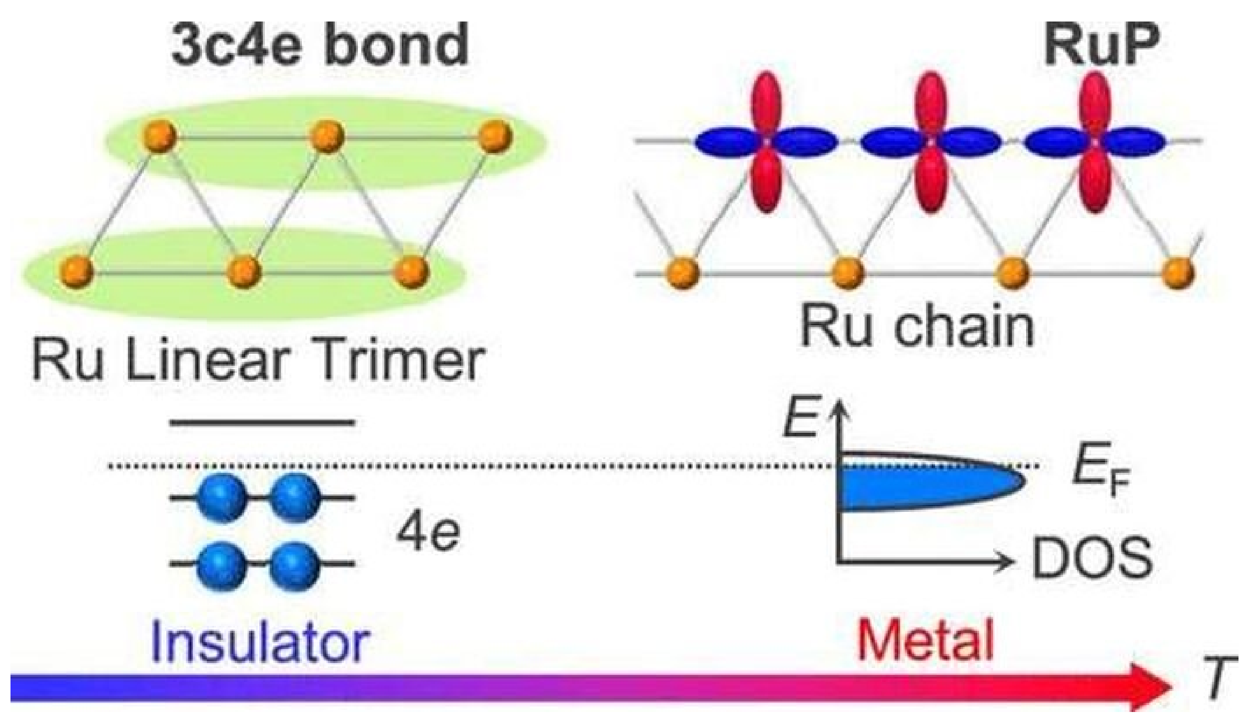

Graphical abstract. Credit: *Journal of the American Chemical Society* (2022). DOI: 10.1021/jacs.2c06173

A group from Nagoya University in Japan has discovered a never-before-seen form of ruthenium phosphide with an unusual configuration of atoms and electrons in its cooled state. This may resolve the puzzle of how a metal can be a conductor at high temperatures, but an insulator at lower temperatures.

Ruthenium is a rare metal that belongs to the platinum group of metals. As a compound, ruthenium phosphide (RuP) is commonly used as a material because of its stability and conductivity. RuP acts like a metal and conducts electricity at room temperature. However, it was discovered in 2011 that when cooled below 0°C, its electrical resistance increases, and it becomes an insulator.

When a metal undergoes the transition from its metallic phase at high temperatures to the insulating phase at lower temperatures, the point when it changes from one to the other is called the metal-insulator transition (MIT). The mechanism by which RuP undergoes this transition, however, has been controversial.

"It has been discussed for over 10 years, but there is no consensus on the mechanism," explains lead author, Associate Professor Daigorou Hirai. "The origin of the transition too has also been a matter of great interest, especially since superconductivity appears when this transition is suppressed."

A group led by Hirai, with Associate Professor Naoyuki Katayama and student Keita Kojima of the Graduate School of Engineering at Nagoya University, investigated the properties and crystal structure of RuP at low temperatures to clarify the mechanism of the MIT using a technique called synchrotron radiation X-ray diffraction. They published their results in the *Journal of the American Chemical Society*.

The group discovered that the uniform distance between ruthenium moleculesatoms found at higher temperatures was modulated as the solid changed from a metal to an insulator. At low temperatures, the crystal forms a structure called a linear trimer that looks like a garden lattice with a series of triangles arranged with their uppermost points pointing up and down and attached in a straight row.

A different type of molecule from those conventionally found in solids, RuP trimers form chemical bonds by incorporating four electrons as they enter the low-temperature phase. This may help resolve the puzzle of how a metal can be a conductor at high temperatures but an insulator at lower temperatures. Electrons are important for the flow of electricity, so when these are captured to make these triplet molecules, it impedes the flow of electricity.

"We discovered that ruthenium switches from a metal to an insulator by connecting three molecules atoms in a straight line and capturing electrons," Hirai explains. "The new type of molecule is composed of three atoms connected by four electrons, whereas most molecules found in solids so far have been composed of two atoms connected by two electrons. Molecules come in a wide variety of shapes and bonding types, but there have been few known variations in solids. Molecular orbitals found in RuP are important in that they show that there is diversity in molecular formation, even in solids."

The formation of molecules in solids, which transforms their electrical and optical properties, can apply to sensors and switching devices. But the team's findings expand that direction of research. "The discovery of various types of molecules can enable more rapid changes in properties, faster responses, and molecular control using magnetic, electric, and stress fields," Hirai explains.

"The formation of the molecular orbital significantly changes electrical conductivity, which can be used as a temperature sensor. Additionally, since the formation of molecular orbitals significantly changes light transmittance, we are also considering smart windows that change light transmittance depending on temperature."

More information: Daigorou Hirai et al, Linear Trimer Molecule Formation by Three-Center–Four-Electron Bonding in a Crystalline Solid RuP, *Journal of the American Chemical Society* (2022). DOI: 10.1021/jacs.2c06173

Provided by Nagoya University