

Scientists Create ‘Light Tweezers’ to Study the Electronic Properties of Solids

Many techniques are currently available to investigate electronic properties – such as conductivity and magnetism – of solids, but for materials made up of different chemical elements, the contributions of the electronic properties of the atoms of each element are difficult to distinguish. Now, a team of scientists has perfected a new technique that does just that.

The scientists have been working on the technique, called site-specific x-ray photoelectron spectroscopy, for the past two years, and have recently used it to investigate the electronic properties of oxygen and titanium atoms in rutile, a mineral made of titanium dioxide usually with a little iron, and used to accelerate chemical reactions. The results of the study, reported in the August 12, 2002 issue of *Physical Review Letters*, represent the first experimental application of the technique to a metal oxide, thus paving the way to understanding the properties of more complex

metal oxides used in the chemical and electronics industry.

“Our technique can unambiguously determine the individual contributions of either the titanium or the oxygen atoms to the electronic structure of rutile,” says physicist Joseph Woicik, of the National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland, and the lead author of the study. “In contrast, other techniques describe the electronic structure of rutile as a whole, which does not say much about how titanium and oxygen atoms interact with each other.”

Picking Different Atoms With Optical “Tweezers”

The new technique, which combines two widely used techniques, called photoelectron spectroscopy and x-ray diffraction, works as follows: Very intense x-rays are first projected towards the material and then deflected by the atomic planes

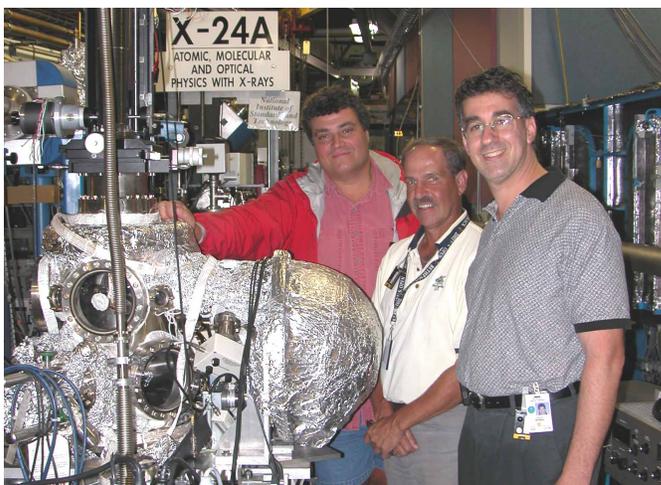
of the material, creating “diffracted” x-rays. When the incident and diffracted x-ray waves combine, they form a standing wave, which is used to excite electrons inside the material. The period of the standing wave, which is the distance between two crests, can be made equal to the distance between two atoms of a given element. As a result, the crests of the wave selectively excite the electrons of the atoms of a given element, but not the electrons of the atoms of other elements. The crests of the standing wave can then be moved in a controlled fashion, thereby allowing them to stimulate electrons of the other elements’ atoms at will.

To study the electronic properties of titanium and oxygen atoms in rutile, Woicik and his colleagues used x-rays generated by the NSLS.

“Because the waves have the same period as the inter-atomic distance, we can selectively excite either the titanium atoms or the oxygen atoms,” Woicik says, “and when one of these atoms is excited, all the other atoms of the same element are excited at once.

“The crests of the standing wave act like tweezers that reach in and pick out electrons,” Woicik says. “The advantage is that you know that the electrons you are studying are coming from either the titanium or the oxygen, but not both.”

The scientists analyzed the energy of the ejected electrons to gain information about the electrons’ positions and energies in the crystal before the electrons were excited.



At beamline X24A (from left to right): Physicist Joseph Woicik (lead author), beamline technical support Barry Karlin and physicist Lonny Berman (co-author). (courtesy of Daniel Fischer, NIST).

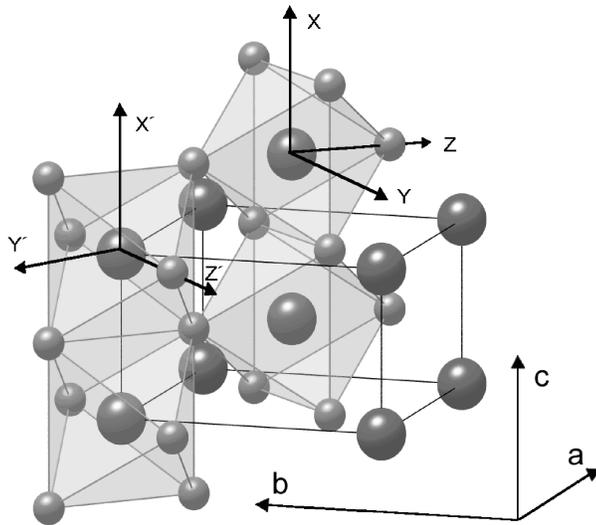


Figure 1: Crystallographic structure of rutile. Titanium atoms are represented by large spheres and oxygen atoms by small spheres.

The analysis was performed with a state-of-the-art device called an electron analyzer, and ultra-high vacuum tools specially designed and built by scientists from the University of Rhode Island in Kingston, the NSLS, and NIST, working at NSLS beamline X24A.

Covalent Bonds and Electric Insulation

By closely looking at the positions of the electrons, Woicik and his colleagues found that the binding of the titanium and oxygen atoms does not follow the more conventional ionic picture, in which the electrons responsible for the binding hover around oxygen atoms but not titanium atoms. The new study shows that, instead, titanium and oxygen atoms share their electrons, making "covalent" bonds.

"We were surprised to notice such a substantial electron density coming from the titanium atoms," Woicik says. "This means that electrons are present around the titanium atoms, which shows that the bonding is covalent."

The researchers also examined the positions of electrons responsible for the conducting or insulating properties of a solid. In the case of rutile, they found that the electrons with the highest energies are not jumping between the atoms, as would be expected in a conductor, but are localized around the oxygen atoms, justifying that rutile is an insulator.

Unexpected Experimental Results

The new experimental results nicely agree with theoretical expectations. But this agreement came as a surprise. Last year, Woicik and his colleagues were testing their technique on copper when they discovered that "valence" electrons, which are peripheral to the nuclei, displayed emission patterns similar to "core" electrons, which are localized close to the nuclei.

"We could not believe what we were seeing," Woicik says. "Because valence electrons are free to roam in between atoms, there was no reason that their emission patterns

would be the same as those of core electrons."

Half convinced that their presumptions might be incomplete, the scientists considered more carefully the nature of the electron waves within the crystal. "Our presumptions were wrong," Woicik says. "Only when the valence electrons are near the cores can they be excited by the x-rays."

These observations demonstrated that the scientists need to consider only the contributions from the individual atoms. "The technique truly works like tweezers that only reach in and grab the electrons in the immediate vicinity of each atom," Woicik says. "This was the

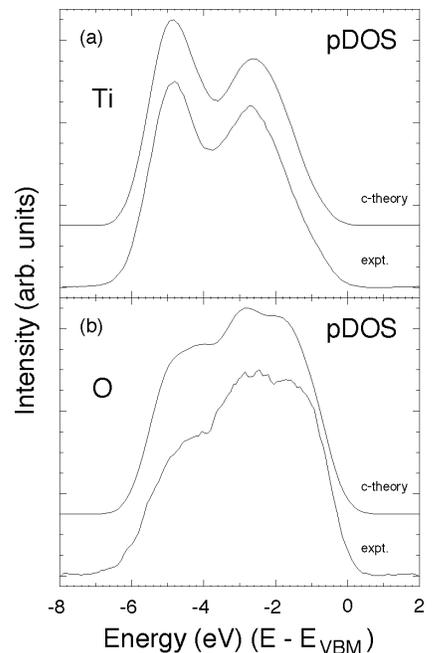


Figure 2: Comparison of theoretical and experimental densities of states of electrons surrounding the titanium (top) and oxygen (down) atoms. The experimental curves, which were obtained from the site-specific x-ray photoelectron spectroscopy technique, agree nicely with the theoretical curves, attesting for the ability of the technique to act as "light tweezers," picking out either the titanium or oxygen atoms.

most startling observation that I have ever made in 13 years working in this field.”

More Results to Follow

The researchers are now interested in applying their technique to more complex metal oxides than rutile, including materials in which electrons interact collectively, a phenomenon responsible for superconductivity – electrical conductivity without energy loss below a certain temperature. The technique could also be used to shed light on the magnetic properties of materi-

als by looking at the magnetic properties of individual nuclei and electrons.

“The beauty of our technique is that it can unravel the electronic structure of simple metal oxides in a way similar to the way you peel an onion,” Woicik says. “By looking at how electrons interact with each other, you can then make more sense of the electronic properties of more complex metal oxides and possibly address intriguing phenomena such as high-temperature superconductivity and metal-insulator transitions.”

BEAMLINE

X24A

PUBLICATION

J.C. Woicik, E.J. Nelson, L. Kronik, M. Jain, J.R. Chelikowsky, D. Heskett, L.E. Berman, and G.S. Herman, “Hybridization and Bond-Orbital Components in Site-Specific X-Ray Photoelectron Spectra of Rutile TiO_2 ”, *Phys. Rev. Lett.* **89**, 077401 (2002).

-Patrice Pages