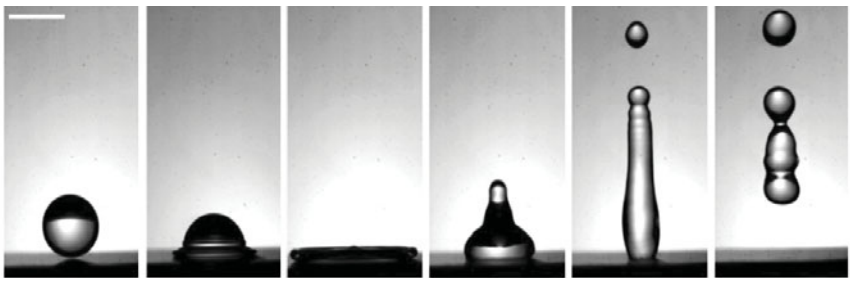
Rare-earth oxide ceramics found to be robustly hydrophobic

Understanding and controlling the hydrophobicity/-philicity of surfaces is critical for a range of applications. Traditional hydrophobic surfaces consisting of a polymer coating over a roughened surface often deteriorate in harsh environments, giving rise to increased wettability. Recently, however, researchers from the Massachusetts Institute of Technology (MIT) have shown that a series of rare-earth oxides ceramics (REOs) are intrinsically hydrophobic, a property related to unique structuring of water molecules at the oxide surfaces.

As described in the January 20 online edition of *Nature Materials* (DOI: 10.1038/NMAT3545), G. Azimi and co-workers sintered REO pellets of the lanthanide series including ceria and lutecia. Upon subjecting them to thermal and abrasive testing, the REOs show minimal change to their hydrophobic nature. Superhydrophobic surfaces were generated by texturing the REOs using a range of techniques, such as sputter-coating onto smooth and microstructured silica surfaces. Contact angles as large as 160° were measured and video snapshots of water droplets falling onto the microstructured surface show the droplets bouncing off the surface.



Sequential snapshots of a water droplet impinging on a surface coated with a thin layer of ceria (~200 nm thick); the droplet cannot form hydrogen bonding with the REO and surface tension causes the water droplet to bounce off the coating illustrating the superhydrophobic nature of these materials. Scale bar 2.5 mm. Reproduced with permission from *Nature Mater*. (DOI: 10.1038/NMAT3545). © 2013 Macmillan Publishers Ltd.

The origin of the hydrophobicity of the REOs can be attributed to their electronic structure. While most ceramics and metals are hydrophilic, due to coordinative unsaturation which allows water to form bonds with available valence orbitals, the 4*f* orbitals of rare-earth atoms are completely shielded by the electrons in the filled 5*s* and 5*p* orbitals. They are thus not available to hydrogen bond with water molecules. This causes the water adjacent to the REO surface to exhibit a hydrophobic hydration structure.

This work highlights the flexibility and scalability of these intrinsically hydrophobic REOs, where they can be fabricated using standard ceramic processing methods. The research also addresses problems of robustness, and may lead to new hydrophobic applications in harsh environments.

Christopher J. Patridge

Energy Focus

Charge-density waves may be competing with superconductivity

Researchers have been trying to identify the mechanisms underlying high-temperature superconductivity (HTS) in cuprate superconductors, typically attributed to charge-density waves (CDWs). Researchers at the Massachusetts Institute of Technology (MIT) and Brookhaven National Laboratory (BNL) have revealed that CDWs cannot be the root cause of the unparalleled power conveyance in cuprate HTS materials. In fact, CDW formation is likely an independent and competing instability according to the researchers, as reported in the February 24 online edition of *Nature Materials* (DOI: 10.1038/NMAT3571).

In describing charge-density waves, co-author Ivan Božovíc of BNL said, "They resemble waves rolling across the surface of a lake under a breeze, except that instead of water, here we actually have a sea of mobile electrons." Once a CDW forms, the electron density loses uniformity as the ripples rise and fall. Detecting CDWs typically requires high-intensity x-rays, but even then, the technique works only if the waves are essentially frozen upon formation. However, if CDWs actually fluctuate rapidly, they may escape detection by x-ray diffraction, which typically requires a long exposure time that blurs fast motion.

For their experiment, the researchers grew thin films of $La_{1.9}Sr_{0.1}CuO_4$, a HTS cuprate compound. The metallic cuprates, assembled one atomic layer at a time, are separated by insulating planes of lanthanum and strontium oxides, resulting in a quasi-two-dimensional conductor. When cooled down to less than 100 K, electron waves began to ripple through the 2D matrix. At even lower temperatures, these films became superconducting.

To catch CDWs in action, the research group at MIT, led by Nuh Gedik, used an advanced ultrafast pump-probe spectroscopy technique. Intense laser pulses, "pumps," cause excitations in the superconducting films, which are then probed by measuring the film reflectance with a second light pulse. The second pulse is delayed by precise time intervals, and the series of measurements allows the lifetime of the excitation to be determined. In a more sophisticated variant of the technique, the researchers replaced the standard single pump beam by two beams hitting the surface from different sides simultaneously. This generated a standing wave of controlled wavelength in the film, but it disappeared

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rapidly as the electrons relaxed back into their original state.

The researchers applied this technique to the $La_{1.9}Sr_{0.1}CuO_4$ films synthesized at BNL. In films with a critical temperature of 26 K, the researchers discovered two new short-lived excitations—both caused by fluctuating CDWs. The new pulse-pump technique allowed the researchers to record the lifetime of CDW fluctuations, which is just 2 ps under the coldest conditions, becoming briefer as the temperatures rose. These waves then vanished entirely at about 100 K, actually surviving at much higher temperatures than superconductivity.

The researchers then hunted for those same signatures in cuprate films with slightly different chemical compositions and a greater density of mobile electrons. "Interestingly, the superconducting sample with the highest critical temperature, about 39 K, showed no CDW signatures at all," Gedik said.

The consistent emergence of CDWs would have bolstered the conjecture that they play an essential role in HTS. Instead, the research team's detection of such electron waves in one sample but not in another (with even higher critical temperature) demonstrates that another mechanism may be driving the emergence of HTS in cuprate superconductors.

Nano Focus

Superdiffusive electron transport mediates laser-induced demagnetization

The mechanics of laser-induced demagnetization has attracted considerable attention in efforts to develop fast-switching optomagnetic logic devices. A femtosecond laser pulse for instance can demagnetize a ferromagnet within a few hundred femtoseconds. Various theories have been proposed to explain how an ultrafast laser pulse can demagnetize a magnetic thin film, ranging from indirect spin-flip scattering to direct laser-induced spin flips. Now, A. Eschenlohr, M. Battiato, and colleagues at Helmholtz Zentrum Berlin and Uppsala University propose that a novel mechanism of superdiffusive electron transport drives the demagnetization.

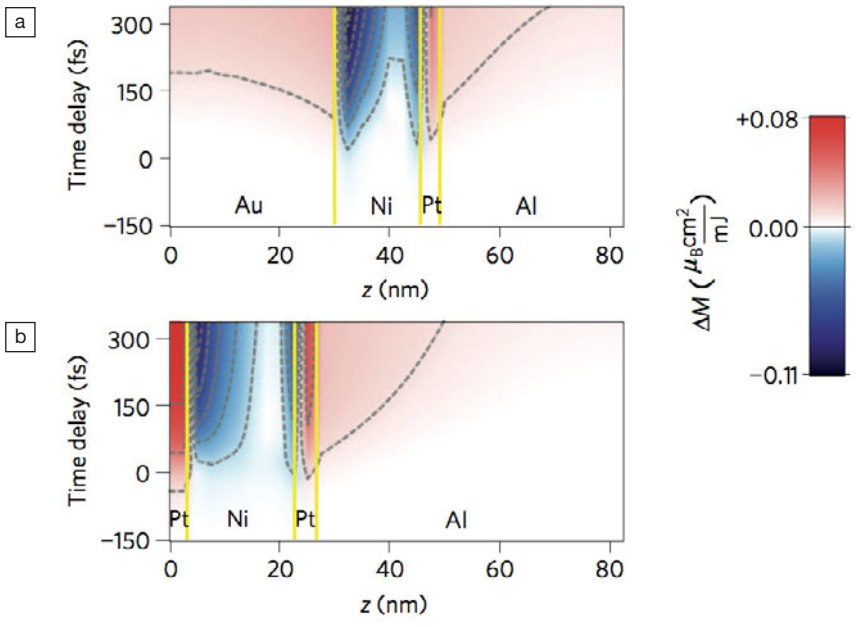
In the January 27 online edition of *Nature Materials* (DOI: 10.1038/NMAT3546), the researchers describe a unique pump-probe study to explore magnetization dynamics in Ni films. They first deposited Au/Ni/Pt/Al and Pt/Ni/Pt/Al multilayers using magnetron sputtering. The former film was grown with a Au capping layer thick enough to absorb almost all the laser light, while the latter features a very thin Pt capping layer. The top layer of the samples was irradiated with a 50 fs laser pulse and the Ni magnetization was measured in a pump-probe fashion using x-ray magnetic circular dichroism (XMCD) to probe the Ni response element-selectively.

The results were modeled using superdiffusive transport theory, which allowed the researchers to extract the spatial and temporal dependence of magnetization in each sample. The results show that in the Au / Ni sample, the spin-majority electrons are mostly conducted from the Ni to the substrate and the Au cap, while spin-minority electrons remain largely trapped in the Ni layer. This leads to a very efficient and ultrafast demagnetization of the Ni layer, which is almost as fast as the response of the Pt/Ni sample measured in parallel.

From these results, the researchers conclude that direct optical excitation does not need to occur for the demagnetization process to take place. This also precludes spin flips as the dominant mechanism for demagnetization, at least for the Au/Ni structure.

The researchers conclude that the model of laser-induced spin transport best describes their demagnetization process. This new understanding may help scientists design a new generation of ultrafast optomagnetic memory materials.

Steven Spurgeon



Schematic of the temporal dependence (vertical axis) and spatial dependence (horizontal axis) change of magnetization (color) in the (a) Au/Ni and (b) Pt/Ni films. Spin-minority carriers (blue) remain trapped in the Ni layer, while the spin-majority carriers (red) are conducted to the substrate. The two samples behave similarly, demonstrating that direct optical excitation is not a requirement for the demagnetization process to occur. Reproduced with permission from *Nature Mater.* (DOI: 10.1038/NMAT3546). © 2013 Macmillan Publishers Ltd.

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