Ferroelectric-like phase transition observed in a metal

The phenomenon of ferroelectricity, in which a compound exhibits a spontaneous electric polarization, is generally thought to be incompatible with metallicity. This seems intuitive, since unbound carriers would quickly act to screen any polarization in a metal. In a strange twist, researchers Youguo Shi of the National Institute for Materials Science in Ibaraki, Japan, and co-workers from China, Japan, and the United Kingdom, now report a ferroelectric-like transition in metallic LiOsO₃ at 140 K. Their results open the door to an entirely new class of materials and shed light on fundamental electron behavior in ferroelectrics.

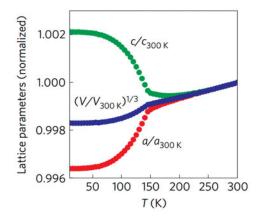
Writing in the November issue of *Nature Materials* (DOI: 10.1038/ NMAT3754; p. 1024), the researchers describe structure refinement studies of

Vanadium oxide metamaterial structure appears to cool as it heats

When an object is heated, it gets hotter and emits more thermal radiation, right? Well, not always. Researchers at Harvard University have developed a thin-film/substrate structure that emits decreasing amounts of thermal radiation when heated over the temperature range of 75–85°C. Viewing this process through an infrared camera, the object appears to be getting colder even though it is really heating up.

Mikhail Kats, a graduate student in the group of Federico Capasso at Harvard University, calls this phenomenon "a very unusual situation—almost pathological." He explains that the amount of radiation emitted at all frequencies from an object at temperature T (Kelvin scale) is proportional to its emissivity times T^4 . "So the only way you can see the effect that we saw is if the emissivity goes down faster than T^4 goes up." This is a huge change in rhombohedral LiOsO₃. Using neutron powder diffraction, they find that this compound forms a LiNbO₃-type crystal structure; at room temperature, it can be described by a centrosymmetric $R\overline{3}c$ space group, which is not compatible with ferroelectricity. However, upon cooling below 140 K, the structure undergoes a phase transition to a noncentrosymmetric R3c space group, which is compatible with ferroelectricity. The researchers confirmed this symmetry change using convergent-beam electron diffraction.

Interestingly, they find that the material remains a metal through the phase change, and they find no associated change in magnetic behavior across the phase transition. This suggests that the transition to ferroelectric behavior in this compound is driven by a displacive, order-disorder-type transition, rather than collective electron motion. The group said that their study may guide other researchers as they seek to



Temperature dependence of the LaOsO₃ unit cell parameters as it undergoes a structural transition at 140 K. Refinement of this structure demonstrates a transition to a noncentrosymmetric space group. Reproduced with permission from *Nat. Mater.* **12** (2013), DOI: 10.1038/NMAT3754; p. 1024. © 2013 Macmillan Publishers Ltd.

understand high-temperature ferroelectric transitions in related LiNbO₃ and LiTaO₃ compounds.

Steven Spurgeon

emissivity. The structure that shows such dramatic properties is a thin (150 nm) film of VO_2 on a sapphire substrate.

"Vanadium oxide is extremely special because the insulating and metallic phases have very different dielectric properties that give you these spectacular changes in the interaction with radiation over very small temperature windows," said Shriram Ramanathan, a Harvard faculty member and co-author of the research published in the October–December 2013 issue of *Physical Review X* (DOI: 10.1103/ PhysRevX.3.041004; 041004).

Scientists have long known that VO₂ undergoes an insulator-to-metal transition (IMT) at 67°C in the bulk material, and they are exploring this phase transition as an on/off switch for optical and electronic applications in thin-film form. But by observing the transition from insulator to metal slowly, in steps of 0.5° C, and in the particular configuration of a thin film of VO₂ on sapphire, Kats, Ramanathan, Capasso, and their colleagues were able to observe this unusual negative differential thermal emittance phenomenon in great detail.

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As the VO₂ thin-film/sapphire substrate heats up in the phase transition region, small islands of metal begin to form in the insulator matrix, forming what the researchers call a "naturally disordered metamaterial." At one point in the phase transition, a lot of IR absorption is exhibited and hence a lot of emissivity, Kats said, while at a point further along in the phase change less IR absorption occurs and therefore less emissivity. Thin-film interference causes incoming infrared radiation to bounce back and forth between the VO_2 thin film and the sapphire substrate, making both components essential in causing the negative differential thermal emittance.

So instead of artificially combining a metal with an insulator in the manual construction of a metamaterial, the researchers have found a way to do this more naturally. "You don't have to pattern very complicated features, and you don't need to worry about mixing and matching composite materials," Ramanathan said. "It's a powerful way to think about designing metamaterials by exploiting electronic disorder at the appropriate length scale."

Like other metamaterials that have been touted for their ability to hide or camouflage an object, it is possible that this VO₂/sapphire structure could be used as a coating on a tank, for example, to make it blend in with the landscape surrounding it. A tank that would normally show up easily in an IR camera because it is hotter than its surroundings might be made to blend in by using a little bit of heat to drastically change its IR emissivity and make the vehicle look colder in an IR camera. Kats has also proposed the possibility of making a rewritable IR "blackboard" held at a temperature within the IMT range. A laser beam or soldering iron could be used to write a message on the blackboard by changing the local emissivity; the message could only be seen by thermal imaging, and would be invisible to the naked eye. Temperature control of satellites in space, where the only way

an object can heat up or cool down is by absorbing or emitting radiation, is another possible application down the road.

Kats talks about future plans to modify the VO₂ or change the substrate to produce a whole family of structures that could be effective in different circumstances. "We need to be able to do this either over a larger temperature range or at lower temperatures," he said. "If you want to put this on a person for temperature regulation or for camouflage, you need to do it not at 75°C but 35°C. A lot of this is going to depend on how we can control the system to change the transition temperature."

According to Richard Haglund, Professor of Physics at Vanderbilt University who was not involved in this research, "This paper suggests a broad applications potential for tunable thermo-optical systems based on the complementary properties of a phase-changing film and an appropriately selected or designed substrate. Given the potential of the VO₂-sapphire system for infrared tagging, camouflage and identification schemes, and the range of possibilities for designer film-substrate systems with specific thermo-optical properties, this paper may well turn out to be Reference Number 1 in many papers yet to come."

"I think that one of the most clever things about this work is that this team saw that the transition region, instead of being a necessary bridge from insulator to metal, could be a region with a wealth of really interesting physics," said Dan Wasserman, an assistant professor in Electrical and Computer Engineering at the University of Illinois at Urbana-Champaign. "The idea of a naturally occurring, and dynamic, disordered metamaterial is fascinating, and they've utilized this transition region to show some really interesting macroscopic features of the material. I look forward to seeing what happens as they continue to explore this material system, in particular at the nanoscale."

Tim Palucka

Nano Focus

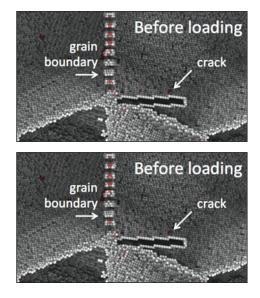
New mechanism heals nanocracks in metal under tensile stress

When a crack forms in a material, typically it is downhill from there onwards. Any further tension makes the crack spread and only increases the damage. At least, that is what intuition and conventional fracture mechanics indicate. Now, the opposite effect has been observed. Under certain circumstances, applying tension or other loading to cracks can actually trigger these fissures to close.

"This really turns our understanding of what is possible in fracture mechanics on its head," said Michael Demkowicz, an assistant professor of Materials Science and Engineering at the Massachusetts Institute of Technology and co-author with graduate student Guoqiang Xu, of an article published in the October 4 issue of *Physical Review Letters* (DOI: 10.1103/ PhysRevLett.111.145501; 145501). "It's not surprising if a crack closes under compression, but if you pull on the crack and see it close, that's very unexpected."

Demkowicz and Xu stumbled across this discovery by accident. While studying hydrogen embrittlement in nickel-based superalloys as part of a project on deepsea oil well applications, they noticed that one of their simulations was behaving in a counterintuitive way. Rather than spreading, the nanocracks they observed seemed to be healing. The researchers assumed there was a mistake with the program or in their parameters, so they combed over the setup for any possible glitches. "We went back and eliminated all of those options," Demkowicz said. "Eventually, we convinced ourselves that it was really happening."

The challenge, then, was to figure out why this was happening. Xu and Demkowicz created detailed computer models simulating how the microstructure of nickel behaved under a number of conditions. Disclinations—a somewhat exotic class of string-like, one-dimensional defects that form in metal but have a much stronger internal stress field than the more common dislocations—turned out to be



Molecular dynamics simulation of nanocrystalline Pd, where a grain boundary migrates under shear stress and heals a crack. Pure shear loading would neither close nor open the crack in the absence of grain-boundary migration. Credit: Guoqiang Xu.

responsible, based upon quantitative measurements of the strength of the stress field. The stress field intensity causes the