

### Nano Focus

#### Tellurium binds bismuth-telluride and gallium-arsenide thermoelectric material

**B**ismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) and gallium arsenide (GaAs) make quite a pair, combining to form a highly efficient electronics-cooling thermoelectric material. Although scientists have been using this material pair for years, how the two materials stick together has remained a mystery. Now, with the aid of high-powered, highly sensitive imaging systems, researchers at North Carolina State University have found a definitive answer.

Most inorganic compounds are held together with chemical bonds, says James LeBeau, a professor of materials science and engineering at North Carolina State University. But for some time, scientists have known that  $\text{Bi}_2\text{Te}_3$  and GaAs do not follow this pattern. Instead, the two materials combine through van der Waals interactions that are considerably weaker than a chemical bond. Just how the bond is formed and how it manages to hold the system together was the real mystery, says LeBeau.

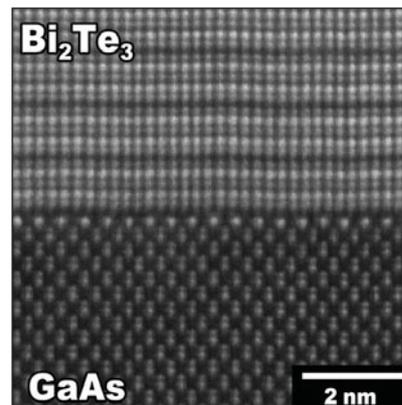
Solving the mystery was a difficult task. Identifying the van der Waals connection between two thin sheets of materials required instrument resolution higher

than most standard systems could provide. LeBeau and his team combined an atomic-resolution aberration-corrected scanning transmission electron microscope (STEM) with a high-powered atomic resolution x-ray spectroscopy system. Such a combination would theoretically image not only the physical structure of the  $\text{Bi}_2\text{Te}_3$  and GaAs, but also the chemical structure at the binding interface.

Scientists had some suspicions as to what was occurring at the interface. GaAs would have dangling bonds that would prevent van der Waals epitaxy. Therefore, either bismuth or tellurium had to interact. To pinpoint which element was reacting with the GaAs, LeBeau and his colleagues along with researchers from RTI International used a vapor deposition technique. Using GaAs as a substrate,  $\text{Bi}_2\text{Te}_3$  was grown layer by layer.

The results, which were published in *Applied Physics Letters*, were surprising, says LeBeau. The STEM images show that the interface between  $\text{Bi}_2\text{Te}_3$  and GaAs is very bright, suggesting that a heavy element must be settled there. The interpretation of the image, says LeBeau, points to the bismuth interacting with the arsenide at the interface.

However, x-ray spectroscopy told a different story. The chemical makeup at the interface included tellurium, not bismuth.



Electron micrograph of the  $\text{Bi}_2\text{Te}_3$ /GaAs interface. Image credit: James LeBeau.

An ultrathin layer of gallium telluride—less than a quarter the width of a normal GaTe structure—solves the long-standing mystery as to how  $\text{Bi}_2\text{Te}_3$  grows through van der Waals epitaxy into remarkably pristine lattices.

“The crystallography tells us that these materials should not grow nicely on top of one another, but they do,” says LeBeau. “And it’s ultimately because there are no strong bonding forces directly between the substrate and the film that enable that.”

**Meg Marquardt**

#### Resonant inelastic x-ray scattering probes spin excitations in iron-pnictide superconductors

**N**ew high-temperature iron-based superconductors (or iron-pnictides), principally comprising iron-arsenide, iron-phosphor, and iron-selenide alloys, were discovered in 2008. In a move to understand the origins of their behavior, an international group of researchers from the Paul Scherrer Institute (PSI), Harwell Science and Innovation Campus, Chinese Academy of Sciences, the University of Tennessee, and the Leibniz Institute for Solid State and Materials Research has now

found that magnetic interactions are of fundamental importance in their high-temperature superconductivity.

As reported in the February 12 issue of *Nature Communications* (DOI: 10.1038/ncomms2428), the researchers compared a sample of a superconducting material with a sample of the parent material, which is non-superconducting. The base material—in this case a barium-iron-arsenide compound—becomes superconducting when it is doped with a defined quantity of potassium atoms.

The research team was particularly interested in the dynamic magnetic properties of the base materials and superconductors. In order to investigate these properties, they excited magnetic fluctuations in the material samples,

where these are accompanied by a re-orientation of the neighboring electron spins, which extends in a wavelike manner through the sample. In the base material, spin waves are clearly detectable.

The researchers wanted to know if this was also true for the doped material samples. At first sight, one might suspect that the holes would constitute obstacles, breaking the long-range magnetic order of spins and thus strongly attenuating the spin waves. However, the research team found that the spin waves experienced little attenuation in the superconductor, and that they exhibited almost the same intensity as in the base material.

In the experiment, the dynamic magnetic properties of the base material and



the superconductor were examined using resonant inelastic x-ray scattering. In this spectroscopic method, the material being investigated is irradiated with x-rays, which excite spin waves in the sample—and thereby lose energy. “By comparing the energies of the incident

and the outgoing light, one can deduce information on the properties of the spin waves,” said PSI postdoc Kejin Zhou, who conducted these measurements.

It is generally accepted that superconductivity arises through “Cooper Pairs” of two electrons “glued” together.

In a high-temperature superconductor, magnetic interactions could potentially be responsible for binding the electron pairs. “Spin waves are the hottest candidates for this,” said Thorsten Schmitt, leader of PSI’s Spectroscopy of Novel Materials Group.

## Bio Focus

### Shape affects success in DNA nanoparticle therapy

The shapes of nanoparticles can play important roles in determining their uptake by cells, and *in vivo* transport in biomedical applications and gene therapy. Providing a means of regulating the transfer of DNA to target sites *in vivo*, a research group from Johns Hopkins and Northwestern universities, led by Hai-Quan Mao and Erik Luijten, respectively, has now discovered a method to control the shape of condensed DNA-block copolymer nanoparticles, and has shown that this may contribute to the development of a more effective drug delivery system that can be used in treating cancer and other diseases. This study, published in the January 11 issue of *Advanced Materials* (DOI: 10.1002/adma.201202932; p. 227), is also noteworthy because it does not use a virus to carry DNA into cells, an approach which can pose health risks during gene therapy.

The nanoparticles developed in this research are formed by compressing DNA with a block copolymer of cation-

ic phosphoester and polyethylene glycol (PEG) in solvent mixtures with different polarities. Electrostatic neutralization between the DNA and polycation drives the assembly, forming a complex core coated with a protective PEG corona. The solvent polarity dictates the interactions between the solvent and the DNA, the polycation blocks, and the PEG blocks, which in turn influences the condensation state of the complex core. This produces micellar nanoparticles ranging from worm- and rod-like to spheroidal shapes. The dense PEG corona renders the surface of the nanoparticles electrostatically neutral and improves their colloidal stability in serum-containing medium. As a result, these “protected” DNA-compacting nanoparticles are able to evade macrophage clearance, making them more stable after injection into the body.

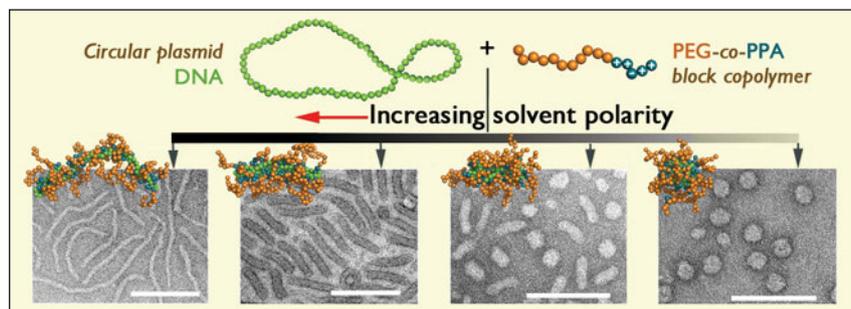
Mao, an associate professor of materials science and engineering in Johns Hopkins’ Whiting School of Engineering, has been developing nonviral nanoparticles for gene therapy for a decade. These particles are designed to deliver their genetic payload only after they have moved through the bloodstream and entered the

target cells. Within the cells, the particle degrades and releases DNA. Using this DNA as a template, the cells can produce functional proteins that combat disease. Mao and his colleagues reported that they were able to “tune” the shapes of the particles, mimicking the shapes and sizes of viral particles. “We could observe these shapes in the lab, but we did not fully understand why the particles assumed these shapes and how to control the process well,” Mao said.

Erik Luijten, associate professor of materials science and engineering and of applied mathematics at Northwestern’s McCormick School of Engineering and Applied Science, led the computational analysis of the findings to determine why the nanoparticles formed into different shapes.

“Our computer simulations and theoretical model have provided a mechanistic understanding, identifying what is responsible for this shape variation,” Luijten said. “We can now predict precisely how to choose the nanoparticle components to obtain a certain shape.” An important finding is that DNA serves as a template for the nanoparticle assembly. In other words, DNA acts both as an active payload and as an important determinant of the overall shape of the nanoparticles.

The researchers also demonstrated the importance of particle shape in actual gene delivery. “The worm-shaped particles resulted in 1600 times higher gene expression in liver cells than the other shapes,” Mao said. “This means that producing nanoparticles in this particular shape could be the more efficient way to provide gene therapy to these cells.” These findings could have important implications to the delivery of other types of drugs as well.



Assembly of micellar nanoparticles with different shapes by condensing DNA with PEG 10K-b-PPA 4K block copolymer in solvents with different polarities. The size markers represent 200 nm. Reproduced with permission from *Adv. Mater.* **25** (2013), DOI: 10.1002/adma.201202932; p. 227. © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.