those given in the international Atomic Mass Evaluation (AME) consortium's most recent (2003) compilation. All three GSI measurements are consistent with the AME masses, which were determined from  $\alpha$ -decay chains. The most striking improvement is GSI's eightfold reduction of the 100-keV uncertainty on the mass of 253No. The earlier uncertainty was so large because <sup>253</sup>No's  $\alpha$ -decay chain involves excited states in fermium-249 and californium-245 whose energies and orderings were unclear. Such troublesome excited states are common in the  $\alpha$  decays of "odd-even" nuclei, with neutron and proton numbers of opposite parity.

The other two isotopes, being eveneven nuclei, don't have that problem. So the uncertainties on their old AME masses were no worse than those of the new Penning-trap measurements. In fact, for <sup>252</sup>No, which had the slowest production rate in the GSI experiment, the 30-keV uncertainty on the new mass is more than twice the AME uncertainty. "Nonetheless," says Block, "the direct weighing of <sup>252</sup>No against <sup>133</sup>Cs already adds reliability to a mass previously known only indirectly, from *a*-particle measurements that might involve significant unknown systematic errors."

The GSI experiment was a proof-ofprinciple demonstration. All three No isotopes had fusion-production rates at least 10 times slower than that of any nuclide previously weighed in a Penning trap. The team hopes soon to reduce uncertainties significantly by raising the overall efficiency, now only about 3%, with which the desired nuclide created in the target makes it all the way through the measurement sequence. An important step will be enlarging and cryogenically cooling the helium gas cell.

## The pairing bonus

To get the nuclear mass from the mass of a neutral atom, one has to consider not only the electron's mass (0.51 MeV) but also its binding energy. In the absence of experimental data, the total electromagnetic binding energy of nobelium's 102 electrons has to be estimated theoretically. But the error on that estimate is presumed to be negligible in the context of the Penning-trap measurements.

The nuclear binding energies, per nucleon, of all three No isotopes are near 7 MeV. With the masses of three adjacent isotopes in hand, one gets their neutron pairing energy  $\Delta_{n'}$  an important quantity for discriminating between nuclear models. Defined as the difference between the mass of the middle nuclide and the mean of the two that flank it,  $\Delta_n$  measures the binding-energy bonus gained by the pairing of outer-shell neutrons. For <sup>252</sup>No–<sup>254</sup>No, the GSI experiment yields  $\Delta_n = +565 \pm 21$  keV. The sign is positive, as one would expect when the middle isotope has the unpaired neutron.

For the superheavy nuclei approaching Z = 118, half-lives get ever shorter and production rates ever slower, eventually precluding mass measurement in Penning traps. But the direct measurement of masses for No and neighbors like rutherfordium (Z = 104) and dubnium (Z = 105) will provide terminal anchor points for  $\alpha$ -decay chains originating as far up as Z = 116. And the demonstration that ions as rare as the GSI nobelium isotopes can be thermalized and trapped should make such exotic species accessible to laser and nuclear spectroscopy.

Bertram Schwarzschild

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# Optical refrigeration sets solid-state cooling record

Certain high-purity solid materials can be cooled by an all-solid-state laser-based system.

**Radiation,** along with conduction and convection, is a form of heat transfer. But in some circumstances, radiation can also induce cooling: Laser light can cool dilute gases of atoms whose thermal energy takes the form of relative translational motion. It can also cool some specially prepared solids whose thermal energy is contained in lattice vibrations.

The basic scheme for optical refrigeration of a solid is shown in figure 1a. A laser excites a transition from an upper level of one state to a lower level of another, and a higher-energy photon is emitted, with phonons making up the energy difference. If the pump light is generated by a semiconductor diode laser, the cooling system as a whole has no moving parts or fluids—a particular advantage for spaceborne applications.

So far, every demonstration of optical refrigeration has used a transparent material doped with a rare-earth element—usually ytterbium, but some studies have used thulium and erbium. The surrounding atoms split the dopant ions' two lowest-energy states into several sublevels, as shown in figure 1b.

Now researchers led by Mansoor

Sheik-Bahae of the University of New Mexico in Albuquerque and Mauro Tonelli of the University of Pisa in Italy have set an optical refrigeration temperature record.<sup>1</sup> They've cooled a solid sample of Yb-doped yttrium lithium fluoride (Yb:YLF) from room temperature to 155 K—about 10 degrees colder than can be achieved by standard thermoelectric Peltier coolers,

previously the best-performing allsolid-state cooling system.

# A balancing act

Each optical absorption–emission cycle extracts only a tiny amount of energy from the sample–at most a few percent of the absorbed photon energy. So for cooling to succeed, several processes that heat the sample need to be kept to



**Figure 1. Optical** refrigeration shown schematically. **(a)** In the general case, the solid sample absorbs a laser photon (black upward arrow) and emits a photon of higher energy (black downward arrow), with phonons (white arrows) making up the energy difference. **(b)** So far, optical refrigeration has

been demonstrated only in solids doped with rare-earth elements such as ytterbium, whose two lowest-energy states are split by the surrounding host atoms into seven sublevels. The intrastate splitting is exaggerated for effect: In Yb-doped yttrium lithium fluoride, the energy difference between levels E4 and E5 is more than 70 times the splitting between E5 and E6.



**Figure 2. Temperatures** achieved (circles) in optical refrigeration of a sample of ytterbium-doped yttrium lithium fluoride, along with model fits (solid lines). Increasing the rate of cooling-by increasing the laser power or bringing the laser wavelength closer to the 1020-nm absorption resonance-decreases the steady-state temperature. The previous optical cooling temperature record (achieved in Yb-doped ZBLAN), the temperature attainable by a solid-state

Peltier cooler, and NIST's definition of a cryogenic temperature are shown for comparison. (Adapted from ref. 1.)

a minimum. First, the transition from excited state to ground state can release phonons rather than photons; just one such nonradiative conversion can undo the cooling of many emitted photons. Fortunately, nonradiative conversion tends to be limited in rare-earth-doped materials, since the key optical transitions occur in the 4f electron shell, which is shielded from the rest of the solid by the 5s and 6s shells. Second, photons can be absorbed by impurities other than the dopant atoms. The magnitude of such parasitic absorption depends, of course, on the sample's purity. Finally, heat is transferred from the environment to the sample at a rate determined by the apparatus design.

At the same time, the rate of absorption–emission cycling must be maximized. That rate depends on the laser power, the dopant concentration, the absorptivity of the dopant atoms at the laser wavelength, and the population of dopant atoms in the upper groundstate levels. As the sample cools, the thermal population of those levels decreases, and cooling slows and eventually stops.

The previous optical cooling record, 208 K, was set in 2005 by Richard Epstein and colleagues at Los Alamos National Laboratory.2 Those researchers used Yb-doped ZBLAN (a glass composed of fluorides of zirconium, barium, lanthanum, aluminum, and sodium), the material in which optical cooling had first been observed.3 ZBLAN's appeal was that it was used in optical fibers, so methods had been developed for synthesizing it to high purity. But its cooling potential is inherently limited. The Yb<sup>3+</sup> dopant takes the place of La<sup>3+</sup> ions, so the dopant concentration cannot exceed the amount of

La<sup>3+</sup> in the glass. And the glass's amorphous structure broadens the Yb<sup>3+</sup> energy levels, so the peak absorption is relatively weak.

# Crystal clear

Because Yb:YLF is a crystal, its Yb<sup>3+</sup> absorption peaks are sharp. And because Yb<sup>3+</sup> replaces Y<sup>3+</sup>, which makes up more than half of the material's mass, much higher dopant concentrations are allowed. But methods for synthesizing Yb:YLF to high purity are not as well developed as they are for Yb:ZBLAN. As Sheik-Bahae explains, apart from the telecom industry, "Nobody else is as interested in that much purity as we are."

In 2007 the Pisa team observed slight cooling in Yb:YLF. The New Mexico researchers-primarily Sheik-Bahae's student Denis Seletskiy-then worked to optimize the conditions for cooling YLF doped with 5% Yb. They enhanced their laser power using an optical cavity. They enclosed their sample in a copper shield to minimize the blackbody radiation absorbed from the environment. And they tuned their high-power laser's wavelength to 1023 nm-as close to the E4-E5 transition's 1020-nm absorption peak as the laser would allow. The temperatures they achieved, monitored by a noncontact method based on fluorescence lineshapes, are shown in figure 2.

The researchers are working on developing a laser that can produce enough power at 1020 nm to excite the E4–E5 transition on resonance. And they think that new crystal-growing processes could produce a Yb:YLF sample that is eight times as pure. Taken together, those improvements could allow cooling to 77 K, the boiling point of liquid nitrogen.

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They've also succeeded in refrigerating a semiconductor by joining it to the Yb:YLF by a thermal link. What they'd really like to do, though, is to cool the semiconductor directly. In that case, the ground and excited states in figure 1a would be the valence and conduction bands. But despite more than a decade of theoretical and experimental research by several groups, net laser cooling of a semiconductor has yet to be observed. **Johanna Miller** 

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# A single-component organic crystal is ferroelectric at room temperature

Hydrogen bonds that hold croconic acid crystals together are responsible for the material's high spontaneous polarization and strong ferroelectric effect.

**Plastics** and other organic materials can be fashioned into bendy, stretchy sheets. Exploiting that flexibility for electronic devices entails finding organics that exhibit useful phenomena. Display panels in cell phones already make use of the semiconductivity and light emission of two organics, polyfluorene and poly(phenylene–vinylene). Ultrathin e-readers are already on the market.

Now, Sachio Horiuchi of Japan's National Institute of Advanced Industrial Science and Technology, Yoshinori Tokura of the University of Tokyo, and their collaborators have found an organic material that exhibits another technologically useful phenomenon, ferroelectricity: the ability to switch polarization in response to an electric field.<sup>1</sup> Ferroelectrics, as well as their cousins, piezoelectrics and pyroelectrics, have a host of applications, including nonvolatile memory, mechanical actuation, and temperature sensing.

The new ferroelectric is the crystalline form of croconic acid, an organic dye first synthesized in 1825 by Heinrich Gmelin. He named his discovery after  $\kappa\rho\delta\kappa\sigma\varsigma$ , the Greek word for saffron. In addition to its industrial uses as a dye, croconic acid is an attractive building block for supramolecular chemistry, the bottom-up self-assembly of nanostructured materials.

Figure 1 shows the structural origin of that attraction and of the solid's ferroelectricity. Each croconic acid molecule consists of a pentagonal ring of carbon atoms bound to oxygen and hydroxyl (OH) groups. The carbon atoms' p orbitals overlap and merge to form  $\pi$  orbitals above and below the ring. The merging weakens the O-H bonds, thereby loosening the hydrogen atoms. In water, the molecules dissolve into  $C_5O_5^{2-}$  anions and  $H^+$  cations—hence the acidity. For supramolecular chemists, the anions' five symmetric, outwardly pointing binding sites turn the anions into tiles that can be assembled into two-dimensional sheets.



**Figure 1. Croconic acid** forms crystals of stacked puckered sheets of hydrogenbonded molecules. (a) Two configurations of hydrogen bond are present, shown here in green and blue. (b) Because of the shape of the molecules and the arrangement of the intermolecular bonds, croconic acid has a spontaneous polarization  $\pm P_{s}$ . Applying an electric field in the right direction can reverse the polarization. (c) The field also changes the bond configuration of each molecule. In some inorganic ferroelectrics, the entire crystal structure breaks symmetry. In croconic acid, only the shuttling H atoms break symmetry. (Adapted from ref. 1.)

In a croconic acid crystal, the loosened H atoms form a network of hydrogen bonds that holds the crystal together. Two orientations of hydrogen bond are present, indicated in figure 1a by blue and green. Crucially, both bond orientations lie more or less in the crystal's ac plane and have a component along the crystal's *c* axis. Moreover, the H atoms lie closer to one molecule, rather than halfway between. An applied electric field has little difficulty shifting the H atoms along the hydrogen bonds to positions on either side of the molecules (see figure 1b-c). Being bound to the strongly electronegative O atoms, the H atoms are partially charged. The ability to shift them sideto-side is what makes croconic acid ferroelectric.

### **Properties**

Despite the straightforward origin of its ferroelectricity, croconic acid was not initially the target of Horiuchi and Tokura's search for organic ferroelectrics. The researchers were exploring a general class of potential ferroelectrics that depend on the shuttling of H atoms between acids and bases. Croconic acid was one of the candidate acids. To learn more about it, they looked up its structure, which had been determined nine years ago by Dario Braga, Lucia Maini, and Fabrizia Grepioni of the University of Bologna in Italy.

The structure suggested that croconic acid might be ferroelectric by itself. Indeed, once Horiuchi, Tokura, and their collaborators had purified and crystallized the compound, they duly found the hysteresis loops of polarization versus electric field that characterize ferroelectrics. Figure 2 shows some examples.

Several aspects of croconic acid's ferroelectricity are noteworthy. At 21  $\mu$ C cm<sup>-2</sup>, the polarization of croconic acid is the highest of all organic ferroelectrics and is comparable to that of barium titanate, an inorganic piezoelectric used in microphones, loudspeakers, and other transducers. Croconic acid's switching field of around 10 kV cm<sup>-1</sup> is also comparable to that of barium titanate; its hysteresis loops ap-