

SCIENCE

Blowing hot and cold

The laser may now nudge materials to radiate and get cooler, says s ananthanarayanan



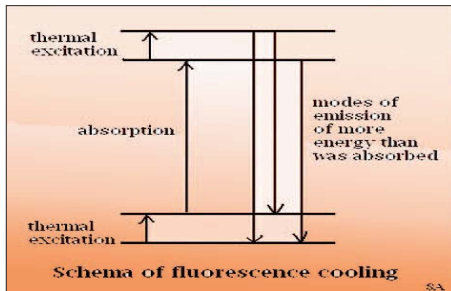
Jun Zhang, Dehui Li, Renjie Chen and Qihua Xiong.

THE laser emits light that is exactly one colour, in a beam that does not spread and, what is basic, light that is not a jumble of photons rushing forth but a regulated stream of waves that are all in step. The laser has found use in communications, in recording and retrieval of data, in research and, thanks to the high power that is possible, it has found application as a source of intense light to create high temperatures. At the other end of the utility spectrum, its property of being accurately at one frequency has made the laser a useful tool to bring about cooling.

The idea of things being induced to radiate and get cooler than the surroundings was proposed many decades ago but could be realised only after lasers came into being, and this was with atomic gases. While some progress has been made with solid materials, there was special interest in laser cooling of semiconductors, which is the material used in transistors and computer chips. Jun Zhang, Dehui Li, Renjie Chen and Qihua Xiong, at Nanyang Technological University, Singapore, report in the journal *Nature* that they have managed just that — cooling nano-ribbons of cadmium sulphide by 40°C below room temperature through the effect of a laser beam at the right frequency.

That hot things radiate heat and cool to the surrounding temperature is obvious. But what we are talking about here is things getting cooler still, by radiating more energy than they receive. Now, the temperature of anything depends on how vigorously its component atoms or molecules are moving or vibrating. On the other hand, absorption and radiation of light takes place by incoming photons energising electrons in atoms, or the emission of photons when the atoms relax. And as the electrons in atoms get more or less energetic in steps of energy, the colours or frequencies of light that is absorbed or emitted by an atom also change in steps and are distinct. But it is interesting that the movement of the atoms themselves can reduce the energy required for an electron transition and allow a weaker photon to excite the electron. When this electron de-excites, this time by the full energy of the transition, the atom emits its characteristic photon and loses more energy than it had gained.

The principle was proposed by a German, Peter Pringsheim, in 1929, in the context of fluorescence, where an atom absorbs light at one frequency and emits light at a lower frequency after disposing of part of the energy in an intermediate transition. Pringsheim proposed that if some of the vibration energy of the atom were consumed in the course of absorbing light, then the final emission would take this energy away and leave the atom with less motion energy than before and, hence, cooler. The principle was practically applied only around 1985, when Stephen Chu, Claude Cohen-Tannoudji and William D Phillips cooled a gas of rubidium atoms with the help of laser light just below the frequency of an electron transition. As atoms of a



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Fluorescence in solids
While speeds of atoms in a gas are high and can ensure selection of only atoms moving towards the laser beam, similar speeds can exist in the lattice vibrations of solids in crystal form. In the case of solids, it is more accurate to say that there are two states, either in the lower or in the higher energy levels, and these two states are separated by a unit of vibration energy of the lattice. A low energy photon can then pump an atom to the higher state after the lower state has received a leg up of vibration energy, or the higher state can de-excite after it rises still higher with the help of vibration energy. In both conditions, emission will carry away some vibration energy and thus cause cooling. The candidate solids for this mechanism fall in two classes. One is a class of metals called transition metals, whose electron configuration has an incomplete inner shell. These atoms allow low energy transitions among the energy levels in the incomplete shell. The other class of solids is the class of semiconductors, where electrons of the outermost shell are loosely bound and can rise, with a small energy jump, to a conduction band. When an electron makes this jump and helps the metal conduct electricity, it leaves behind an atom with one electron short. This missing an electron is called a hole and the pair, of the excited, free electron and the hole, can move rapidly through the metal, treated for

computation as a particle called an excitation.

Fluorescence cooling has been practically realised in the first category — that is, glasses doped with the so-called rare earth metals. Using glass doped with the metal ytterbium, cooling by 110° Celsius has been achieved. While these successes, which are with metals that undergo electron transitions, are of interest in using light for cooling, there is interest in doing the same with semiconductors, where the

transition that would carry away vibrational energy is of the free electron that transits across the band gap that separates it from being a conducting electron. It is just this property that accounts for the value of semiconductors in electronics and a major concern in creating high power

computing devices is finding a way to cool the semiconductor materials.

If there could be a way to use a laser to induce the material to mop up its thermal energy and push it out as radiation, this would open the doors to increasing the dimensions of semiconductor devices. Even lasers themselves, when they are used to create intense beams for use in industry, generate huge heat and the need for cooling is a design limitation. Using part of the laser beam itself to be the cooling agency would similarly enable more powerful lasers.

Semiconductor cooling

But the pursuit of fluorescent cooling of semiconductors with lasers has not been smooth. In principle and in practice, the procedure has worked but real cooling has not been measured. There has been success with the semiconductor gallium arsenide (GaAs), but notable cooling is still not achieved because the material prevents fluorescent radiation from passing out of the material and forces it to get absorbed within the material itself.

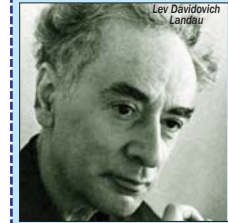
There has also been progress with gallium nitride, awaiting improvement. It is in this context that the work of the Singapore scientists, reported in *Nature*, is significant. The Singapore group used a different category of semiconductor material, cadmium sulphide (CdS), in the form of atom-scale thin ribbons (nanoribbons) and attained a temperature drop of 40° Celsius while working at room temperature, and a drop of 15° Celsius when working at -173° Celsius.

The team attributes the success with cadmium sulphide to the strong interaction of electron-hole pairs and the collective thermal excitation of the lattice of cadmium and sulphur atoms, which brings about a reduction of the latter when a tuned laser photon is absorbed and emitted with higher energy. The team used sensitive measurement of the emitted light to estimate the temperature of the nanoribbons and was able to assess how the cooling depended upon the power and the frequency of the laser light used. Semiconductors with "strong excitation — excitation interaction, of the category of CdS, could perhaps be harnessed to achieve laser cooling and open the way to optical refrigeration based on semiconductors", say the authors of the paper.

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Something for nothing?

FLUORESCENT cooling seems to reverse the order of things in nature. The normal way of nature is that energy is lost to get work done, like a falling stone loses height as it falls faster. Similarly, heat flows from hot to cold for work to be done, like steam condensing in a steam engine, which is a case of using the energy in coal to work



Lev Davidovich Landau.

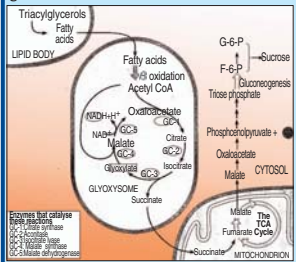
the piston. Conversely, to move heat from cold to hot, we need to do work. In a refrigerator, for instance, electric power has to drive the compressor and take heat from the freezer to the radiator. It has even been proved that the cycle of cooling and reheating is never fully efficient, which is to say that we cannot use a refrigerator to drive a heat engine! But in the case of fluorescent cooling, it looks like a low energy photon steals energy from the substance and exits at a higher energy. Conceivably, this higher energy photon could cool another semiconductor and gain further energy, and so on! Does there seem to be a paradox here? The answer was provided by Landau in 1946, that the secret lies in the loss of order in the laser, which reappears as disordered emitted radiation from the fluorescent material. The increase in order in the material, on getting cooled, is more than the order that is lost by the laser, which starts out with strictly defined frequency, all photons being in step and the beam being accurately directional.

Metabolic lifeline

tapan kumar maitra explains the glyoxylate cycle, glyoxysomes and seed germination

PLANT species that store substantial carbon and energy reserves in their seeds as fats face a special metabolic challenge when these seeds germinate: they must convert the stored fat to sucrose, which is the immediate source of carbon and energy for most cells in the seedling. Many plant species fall in this category, including such well-known oil-bearing species as soyabean, peanuts, sunflowers, castor beans and maize. The fat consists mainly of triacylglycerols (triglycerides) and is stored as lipid bodies, either in the cotyledons of the plant embryo or in the endosperm, the nutritive tissue that surrounds and nourishes the developing embryo.

The advantage of storing fat rather than carbohydrates is clear when you consider that one gram of triacylglycerol contains more than twice as much energy as one gram of carbohydrate. This difference enables fat-storing species to pack the greatest amount of carbon and calories into the least amount of space. However, it also means that such species must be able to convert the stored fat into sugar when the seeds germinate.



The conversion of fat to sugar is not possible for most organisms but that does not mean that it can readily convert sugars and other carbohydrate to stored fat. However, most eukaryotic organisms cannot carry out the reverse process. For the seedlings of fat-storing plant species, though, the conversion of storage triacylglycerols to sucrose is essential because sucrose is the form in which carbon and energy are transported to the growing shoot and root tips of the developing seedling.

The metabolic pathways that make this conversion possible are β oxidation and the glyoxylate cycle. The function of β oxidation is to degrade the stored fat to acetyl CoA, which then enters the glyoxylate cycle, a five-step cyclic pathway, that is named for one of its intermediates, the two-carbon keto acid called glyoxylate. The glyoxylate cycle is related to the TCA cycle, with which it has three reactions in common. There is a critical difference, however: this is reflected by the presence of two glyoxysome-specific enzymes, isocitrate lyase and malate synthase. Using these enzymes, the glyoxylate cycle bypasses the two decarboxylation reactions of the TCA cycle. Also, the glyoxylate cycle takes in not one but two molecules of acetyl CoA per turn of the cycle, generating succinate, a four-carbon compound. Thus, the glyoxylate cycle is anabolic (carbon enters as two-carbon molecules and leaves as a four-carbon molecule), whereas the TCA cycle is catabolic (carbon enters as a two-carbon molecule and leaves as two CO₂ molecules).

In the seedlings of fat-storing species, the enzymes of β oxidation and the glyoxylate cycle are localised in organelles called glyoxysomes. Glyoxysomes are found in the seedlings of fat-storing species and sometimes in senescing leaves. The intimate association of glyoxysomes with lipid bodies presumably facilitates the transfer of fatty acids from the latter to the former.

It brings all the relevant metabolism together in an intracellular context. Storage triacylglycerols are hydrolysed in the lipid bodies, releasing fatty acids. These are transported into the glyoxysome and are degraded by β oxidation to acetyl CoA, which is converted to succinate by the enzymes of the glyoxylate cycle. The succinate moves to the mitochondrion, where it is converted via fumarate to malate by a reaction sequence that is a part of the TCA cycle.

Malate is then transported to the cytosol and oxidised to oxalosuccinate, which is decarboxylated to form phosphoenolpyruvate (PEP) which, in turn, serves as the starting point for gluconeogenesis in the cytosol, ultimately yielding sucrose, the major carbohydrate transported to growing tissues in plants. The route from stored triacylglycerols to sucrose is obviously quite complex, involving enzymes located in lipid bodies, glyoxysomes, mitochondria and the cytosol. But it is the metabolic lifeline on which the seedlings of all fat-storing plant species depend.

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Really, who needs 4G?

david phelan analyses the present and future of speedy mobile data

IN the next few days the airwaves will go on sale and bidding will begin for an auction of so much spectrum, as it's called, that will increase the available airwaves by 75 per cent. This auction is for the frequencies that will underpin the next generation of mobile phones, tablets and more. The process will be powered by a complex and sophisticated piece of software designed specifically for the purpose. But do we need it? What are the benefits? And should we care? Well, for a start, we can have a clear idea of what's coming because one network, EE, has already launched its 4G service. So what was 4G set up to deliver and how is it doing? It came about because we mostly use smartphones now, supplementing calls and texts with obsessively browsing the Internet, checking email and, more of all, consuming apps on the go. We were made to do this thanks to the last auction, for 3G frequencies. That led to the launching of the first 3G network 10 years ago (on 3 March

2003) and other companies following suit. We were promised video calling (which came, but nobody really used it) and fast data connections. Only when the iPhone launched and added the word 'apps' to our vocabulary did 3G data usage really take off. Suddenly, everyone wanted to have the latest currency conversions, stock prices and weather forecasts that speedily data made comfortable. Actually, almost nobody wanted those particular things, but they wanted to be able to get them, just in case. And everyone certainly wanted to be able to tap an address into a map app to see directions on how to reach it. Or speak the name of a nearby restaurant to find its phone number, read reviews and check opening hours. Or use Augmented Reality — where digital effects are overlaid on top of the physical world — the phone's camera can see — to find the nearest Metro station in a deeply cool way. Not to forget Facebook and Twitter posting and checking, iPlayer streaming and YouTube browsing. All very well, but the 3G networks have been cracking with the weight of data traffic for ages now. A YouTube clip uses hundreds of thousands times the amount of data a text message does. Hence the need for 4G, or 4G Long

Term Evolution to give it its full name. There are two bands of airwaves being auctioned in multiple lots. One is low frequency — 800MHz — and will be the most keenly fought over. Mobile signals travel further at lower frequencies so they can penetrate further into buildings and even underground. As Kester Mann, an analyst at CCS Insight, points out, "One of the 800MHz lots will carry an obligation to provide mobile broadband coverage indoors to 98 per cent of the population by the end of 2017". The other frequency is 2600MHz, which won't get inside buildings so easily but will still be in demand. The 4G already available, from EE, is at a frequency in between, 1800MHz, and came about because EE, forged from the familiar and all-too-infringing three mauve dots that appear while the iPhone tries to parody your spoken words into text. Even worse, when it just can't do it, those dots wobble, as if shaking their heads in sorrow. This happens a lot on 3G connections. But if your EE phone says LTE in the top corner, everything flies. Dictation is converted to text often before you've taken the phone from your mouth to see what it's doing. It's spectacularly impressive, and since voice recognition, I predict, is going to



be one of the technologies that comes of age this year, it will be increasingly useful. Similarly, the pleasures of seeing Google searches populating the screen in a grant's crocheted or judder-free video streaming are hard to exaggerate. To be clear, we've been here before — this is the speed and efficiency we were promised when 3G was launched, and my experiments are on a network that isn't yet choked with users. Even so, the speed step-up does seem to be happening this time. Who knows, maybe we'll take up video calling as well. Maybe not.

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