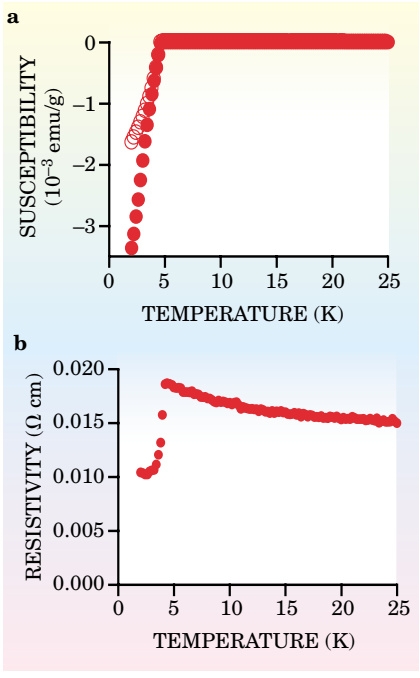

Figure 3. Superconductivity appears in $Na_{0.35}CoO_2 \cdot 1.3H_2O$ below about 5 K. **(a)** Magnetic susceptibility drops precipitously there in the presence and absence of a magnetic field (open and filled circles, respectively). **(b)** Resistivity also falls steeply near 5 K. (Adapted from ref. 2.)

has a spin of ½. When Na atoms are added to this compound, each contributes one electron, thereby changing Co^{4+} to a spinless Co^{3+} state.

The thermoelectric material, with $x \approx 0.7$, has, on average, 30% Co^{4+} and 70% Co^{3+}. To make the superconducting form, Takada and company managed to coax more Na atoms to leave the material and thereby decreased the doping to $x \approx 0.3$. The lighter doping reverses the previous picture so that 70% of the sites are occupied by spins. As holes hop around, the spinless Co^{3+} ions appear to move in a sea of Co^{4+} sites, effectively becoming charge carriers with no spin.

The CoO_2 lattice is known as a Mott insulator—a structure in which each electron is localized on a single site by strong electron–electron interactions. The tendency for nearest neighbors to align their spins in the opposite directions is nearly frustrated by the triangular geometry. This Mott insulator is the starting point for Anderson's RVB model. The resonating bond is the fluctuating singlet pairing of adjacent electrons.

One gets a superconducting state by doping the Mott insulator with Na atoms. If adding Na is equivalent to electron doping, what role is played by the water, which so far seems essential to achieving superconductivity? Experimenters are already trying to answer this question. Some theorists postulate that the water screens Co atoms from the strong Coulomb force of the Na atoms.

The hydrated form of Na_xCoO_2 has been available mostly as a powder and is readily dehydrated in air. A group at Oak Ridge National Laboratory has now shown that one can grow single crystals of the compound by conventional methods.[8] An MIT group recently developed an electrochemical technique that enables them to grow single crystals[9] and to have more precise control over the doping level x. With such improved samples, we can look forward to more definitive results.

Barbara Goss Levi

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Band on the Run: Light Meets Shock Fronts in Virtual Photonic Crystals

When light interacts with dynamically changing photonic structures, the results can be surprising—and in some cases unprecedented.

When the Schrödinger equation is solved for periodic potentials, the allowed energies are confined to a series of energy bands. That predicted energy structure is familiar from metals, semiconductors, and insulators. A similar but less well-known prediction follows when Maxwell's equations are applied to materials in which the dielectric function varies periodically: The frequencies of light that can propagate through the medium are confined to prescribed bands. Light with frequencies in the gaps between those photonic bands reflects off the medium's surface.

Materials with periodic dielectric structures are called photonic crystals, and they have been constructed with periodicities in one, two, and three dimensions. In dimensions greater than one, a considerable challenge is to fabricate structures that block the propagation of light in all directions. The challenge has been met, first by UCLA's Eli Yablonovitch in 1991. Since then, and especially in the past five years, the technology for making dielectric crystals has advanced impressively. Physicists now have a great deal of control over the periodicity of photonic crystals.

Until a few months ago, work on photonic crystals had generally involved static structures with fixed dielectric period. But earlier this year, MIT postdocs Evan Reed and Marin Soljačić, along with group leader John Joannopoulos, investigated materials in which the dielectric function varied with time.[1] In their analytical and computer studies, a shock wave propagated through a one-dimensional dielectric and reduced the period of the dielectric function in the shocked region.

When the MIT group explored the interaction of light with the moving shock wavefront, the results they discovered were quite unexpected. "Who would have guessed," noted Yablonovitch, "that out of plain old Maxwell's equations, so much richness would emerge?"

Ratchets and funnels

Reed and company conducted simulations in which light interacted with advancing shock fronts moving at

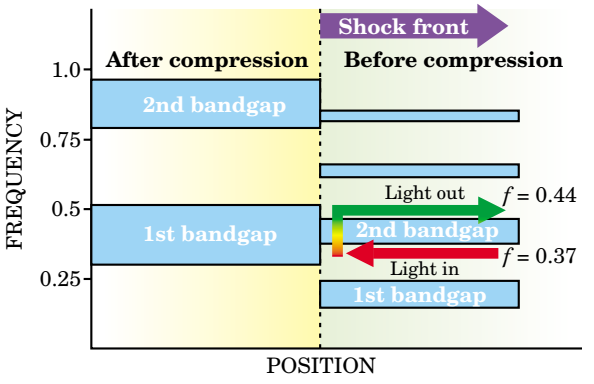

Figure 1. Bands and gaps evolve when a shock wave propagates in a photonic crystal. Simulations reveal that light approaching the shock front with a frequency below the second bandgap can reflect off the shock front with a frequency above the gap. The dimensionless frequency f is measured in units of c/a where a is the pre-shock lattice period and c is the vacuum speed of light. (Adapted from ref. 1.)

roughly 10^{-4} the vacuum speed of light c. The effect of the shock waves was to halve the period of the dielectric function. In some simulations, the light encountered a fixed mirror after reflecting off the shock front.

The simulations offered three surprises. First, the frequency of light increased by almost 20% after the light interacted with a shock front moving at $3.4 \times 10^{-4}\ c$. One expects that light bouncing off an advancing front would be Doppler-shifted up in frequency, but the shift observed in the MIT simulation was almost three orders of magnitude greater than what one would naively predict. A second, related phenomenon is that light was trapped in the vicinity of the shock front for an appreciable time, comparable to the time the shock front took to traverse one period of the dielectric crystal. Third is an effect not seen in other systems: The frequency spread of light bouncing between an advancing shock front and a fixed mirror decreased with time. But the energy in the light beam remained essentially constant. The shock front–mirror system thus acted as a frequency funnel, squeezing light energy into a narrower frequency band.

The essential physics of the frequency shifting and light trapping is displayed in figure 1, which depicts the first two frequency bands and bandgaps for the pre- and post-shock crystal. The MIT group designed their virtual crystals to have the first bandgap in the compressed region overlap with the second bandgap in the region that has yet to be shocked.

Now suppose that the shock front propagates to the right, and consider light traveling to the left with a frequency below the second bandgap of the pre-shock region but within the first bandgap of the region that has been shocked. On encountering the advancing shock front, the light, unable to penetrate the shocked region, will reflect.

The medium's dielectric function, of course, cannot change its period discontinuously. The simulation includes, near the shock front, an interpolating region in which the function smoothly connects two periodic regions. As the light reflects, the bandgaps in the region being compressed evolve upward in frequency. The light is trapped by the stationary first bandgap of the compressed region and the evolving bandgaps.

While trapped, the light constantly bounces off the advancing shock front, and with each bounce, it receives a small frequency kick upward. In the time that the shock front traverses about half an uncompressed dielectric period, the light's frequency shifts above the second bandgap of the pre-shock region, and the light escapes to the right, into the region that's soon to be encountered by the shock front.

Figure 2 shows snapshots of the evolving light. Initially, light with a well-defined frequency approaches the shock front. As the light interacts with the front, the frequency of the light blurs, but generally ratchets upward. The result of the trapping and ratcheting of light is a pulse with a well-defined, raised frequency. Pulses exit at a rate set by the time required for the shock front to travel one lattice period.

The frequency-funneling phenomenon is depicted in figure 3, which has a shock front advancing at $10^{-4}\ c$ toward a fixed mirror. In the simulation shown, the shock front–mirror system reduced the frequency spread of a light beam by a factor of four but did not significantly change the average frequency. However, if the light-beam frequencies were to approach the frequency of a band edge, the beam would experience both an increase and a funneling of frequency.

The large compressions generated in the simulations lead to dramatic effects. But the phenomena also occur—albeit less spectacularly—with much smaller compressions. In addition, in contrast to the frequency increases of light demonstrated in nonlinear sys-

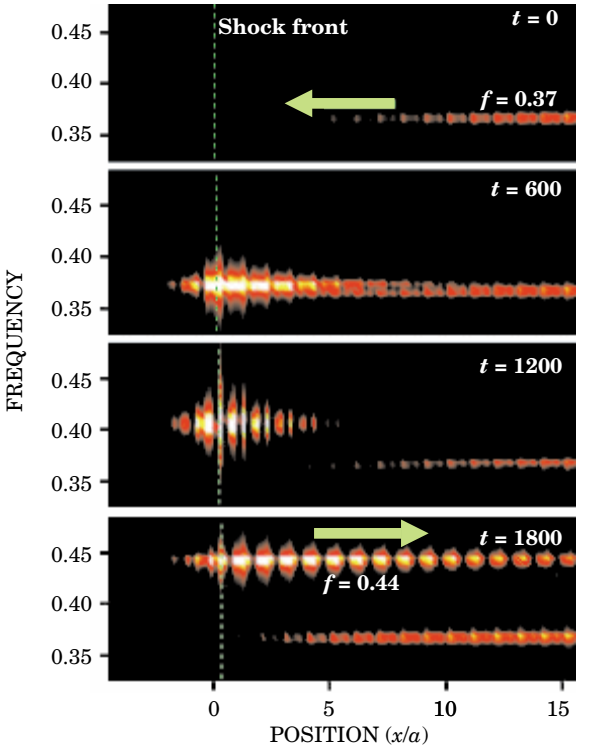

Figure 2. Light is trapped near a shock front as its frequency ratchets upward. The four snapshots here (a short movie appears at http://ab-initio.mit.edu/photons/shocked_PC/3pulse.avi) show the evolution of a light beam encountering a shock front, moving upward in frequency during an interval of time in which it is trapped near the front, and reflecting from the front as a series of pulses. Over the course of this simulation, the shock front moves about half a pre-shock lattice period a. The dimensionless frequency f is measured in units of c/a where c is the vacuum speed of light. The dimensionless time t is measured in units of a/c. The light in the bottom two panels with $f = 0.37$ is a combination of incoming light and reflected light with imperceptibly raised frequency. (Adapted from ref. 1.)

tems, the phenomena observed by Reed and colleagues would be seen with arbitrarily low light intensities. In principle, they'd be obtained in realizations in which light was sent into the photonic crystal one photon at a time.

With a bullet

To date, the phenomena predicted by the MIT team have not been tested experimentally. But Reed, working with Neil Holmes and Jerry Forbes of Lawrence Livermore National Laboratory, is contemplating experiments that may realize the effects seen in the simulations. Reed and his California colleagues plan to use a room-sized gun to shoot a projectile at a multilayer photonic-crystal film. Reed admits the experiment is "literally a one-shot deal." The powerful compressive wave generated in the photonic crystal will destroy the target, although there's plenty of time to gather the necessary data before the crystal disintegrates.

Other methods for compressing photonic crystals are not so violent. Laser or acoustic generation of compressive waves is a possibility. And cleverly designed systems can mimic the effects of compressive waves without the need to physically compress a photonic crystal.

In one scenario, light scatters off a photonic crystal that is rolled into a spiral jellyroll shape and rapidly rotated about the spiral's axis. At first blush, that system looks nothing like the shocked photonic crystal simulated at MIT, but the physics of the two systems is quite similar.

As Joannopoulos explains it, one can think of the compressive shock front as forming the boundary between two photonic crystals with different periodicities. As the front advances over a lattice period, the number of unit cells on the compressed side behind the front increases by one, at the expense of a unit decrease on the front side. The mathematics of the phenomena discovered by the MIT team can be traced to the transfer of cells from one photonic crystal to another.

How is Joannopoulos's explanation related to a jellyroll? Light impinging from a fixed direction on a rotating spiral sees an oscillating number of unit cells, which, in effect, resembles the shunting of cells implemented in the MIT simulation.

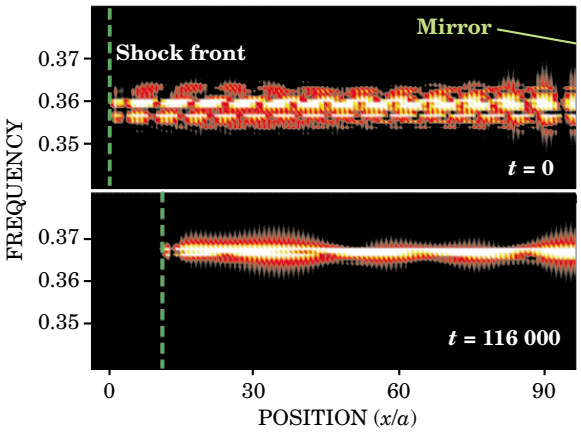

Figure 3. Light bandwidth narrows when light bounces between an advancing shock front and the mirror at the right-hand boundary of this image. Over the course of this simulation, the shock front moves about 10 pre-shock lattice periods *a*, and the frequency band is narrowed by about a factor of four. The dimensionless frequency is measured in units of *c*/*a* where *c* is the vacuum speed of light. The dimensionless time *t* is measured in units of *a*/*c*. (Adapted from ref. 1.)

The phenomena observed at MIT can be tuned by changing parameters such as the lattice period. If they could be realized in a controlled way, the phenomena could see a wealth of applications. The ability to increase light frequency may have applications in FM communications, for example. Or, photonic crystals that trap light could serve as delay-line analogs in computers that rely on photon propagation. In time, solar cells might use band-narrowing devices to efficiently harness the energy of the broad solar spectrum.

In its most recent simulations, the MIT group considered shock fronts that left in their wake not only a change in dielectric periodicity but also changes in the dielectric function due to material strain. The shocks were designed so that, in contrast to the system illustrated in figure 1, the bands in the shock region were lowered compared to their counterparts in the pre-shock region. As a consequence of that novel band evolution, light bouncing off an advancing shock front was shifted to lower frequencies. Such so-called negative Doppler shifts have been predicted for left-handed materials (see PHYSICS TODAY, May 2000, page 17), but the photonic crystals simulated at MIT were not left-handed; the physics leading to the unusual Doppler shifts in the two cases appears to be completely different.

Steven K. Blau

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Watching a Molecule Break Up Reveals How Quickly It Changes Shape

It takes less than 60 femtoseconds for a doubly charged acetylene ion to change into its structural isomer vinylidene.

In papers that dissect the physics of chemical reactions, you'll often find a cartoon. The molecules in the cartoon appear as colored blobs or stick figures. Simple arrows indicate key motions. More succinctly than words or Hamiltonians, the cartoon embodies and conveys what's going on.

Getting to the point where one can draw such a cartoon is an arduous journey. Even for simple molecules whose structures are known, solving the quantum mechanical equations requires months of computer time. It's just as hard in the lab. Between reactants and products lies a host of short-lived quasistable intermediaries whose existence—let alone properties—is difficult to pin down.

But now a team of researchers has taken a different, more direct route to distilling the essential physics of a reaction. Using an innovative spectroscopic method, Timur Osipov of Kansas State University, his thesis adviser Lew Cocke, and their collaborators in the US and Germany have succeeded in tracking and timing how an acetylene molecule changes into its structural isomer vinylidene.[1]

The transformation is simple—the hopping of a hydrogen atom from one carbon atom to another—and the molecule is small. But, says MIT's Bob Field, "It's really an extraordinary accomplishment."

Hydrogen swapping

Acetylene has the chemical formula C_2H_2. Its four atoms are arranged in a straight line: two triply bonded carbons on the inside, two hydrogens on