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Phononic Crystals

by

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and

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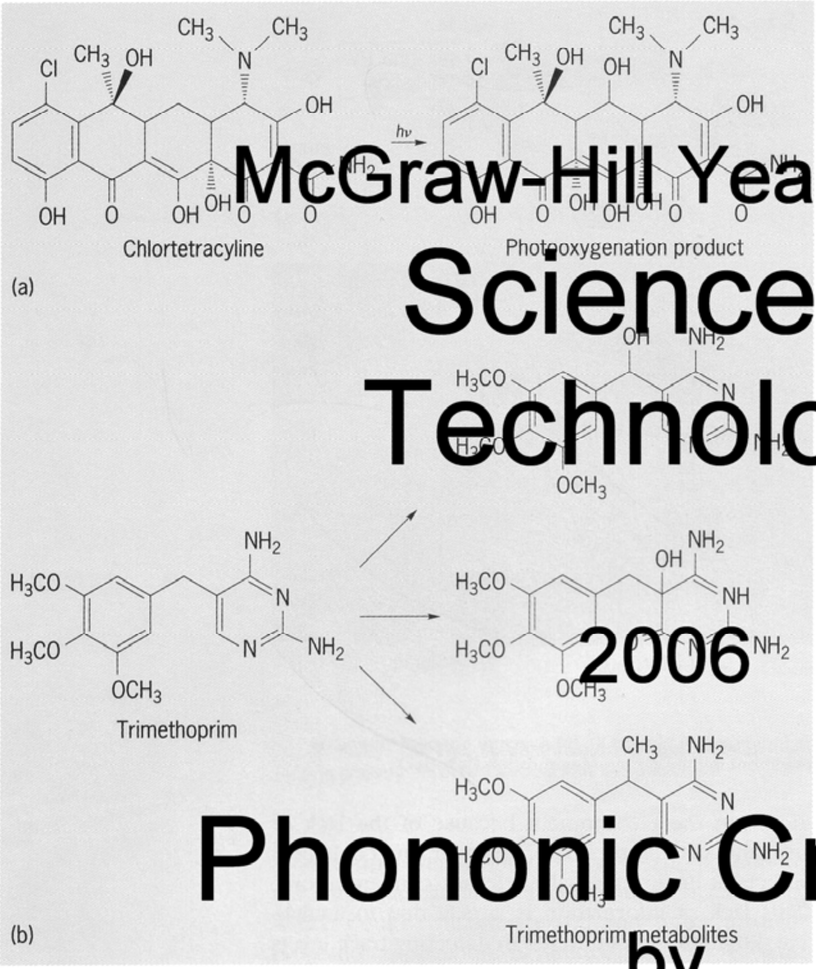

Fig. 5. Reactions showing (*a*) chlortetracycline and its photodegradation product in hog manure, and (*b*) chemical structures of trimethoprim and its metabolites in activated sludge.

time-of-flight mass spectrometer (ToF-MS) has resulted in more degradates and metabolites being identified. These two mass-spectrometric techniques provide complementary data that facilitate structural identification of compounds. For instance, multiple stages of fragmentation in an IT-MS can generate spectra with large amounts of structural information that allow the identification of an unknown degradate. Without multiple stages of mass spectrometry, isomers may not be distinguishable from each other. For example, the protonated molecular ions [mass/charge ratio (m/z) 479] of chlortetracycline and its isomeric conversion product, iso-chlortetracycline, both produce only one fragment ion with m/z 462 corresponding to the neutral loss of NH_3. Isolation and further fragmentation of this ion results in distinct spectra providing valuable structure-specific information (**Fig. 4**).

Further confirmation of the assigned identity or chemical formula of new degradation products can be achieved by accurate mass measurements using ToF-MS. Current benchtop ToF-MS instruments can now achieve low-femtomole-level sensitivity, with high resolving power and mass accuracy. A combination of these mass-spectrometric approaches has been successfully used in the identification of a photooxygenation product of tetracycline in manure and trimethoprim metabolites in activated sludge, with structures shown in **Fig. 5**. Other researchers have also used IT-MS and ToF-MS for effective screening and identification of unknown pharmaceutical contaminants in water.

Recent studies have indicated that some degradation products and metabolites of recalcitrant pharmaceutical compounds are not very different from their parent compounds. For example, the photooxygenation product of chlortetracycline formed at environmentally relevant conditions has a structure that is only slightly modified compared to its parent compound (Fig. 5*a*). Likewise, the metabolites of the antibiotic trimethoprim in activated sludge are also very similar to the parent trimethoprim (Fig. 5*b*), indicating that the absence of the active ingredient of the pharmaceutical from the waste-treatment effluent does not necessarily mean that the compound has been completely eliminated. Knowledge of the nature and quantities of the by-products of degradation or treatment is important because they may also have long-term ecotoxicological effects.

For background information *see* ANTIBIOTIC; BIODEGRADATION; ENVIRONMENTAL TOXICOLOGY; HAZARDOUS WASTE; INDUSTRIAL WASTEWATER TREATMENT; LIQUID CHROMATOGRAPHY; MASS SPECTROMETRY; SEWAGE; SEWAGE SOLIDS; SEWAGE TREATMENT; WATER POLLUTION; WATER TREATMENT in the McGraw-Hill Encyclopedia of Science & Technology.

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Phononic crystals

Phononic crystals are periodic composite materials made from constituents with different densities and acoustic wave velocities. These synthetic materials, which are analogous to photonic crystals for electromagnetic waves, are of growing interest because they can change the way in which sound or ultrasound travels through matter, leading to a number of novel applications. Phononic crystals may be constructed by arranging identical objects [for example, rods in two dimensions (2D) or spheres in three dimensions (3D)] in a regular periodic array or crystal lattice, and embedding these elementary units in a host material or matrix. The key feature of phononic crystals is their periodicity, which causes the propagation of acoustic or elastic waves to be dramatically modified when length scale of the periodicity is comparable with the wavelength of sound (or ultrasound). The origin of these effects is the interference of waves scattered from the periodically arranged constituents. The overall size of phononic crystals may vary from several meters down to several micrometers, depending on the size of the elementary units (such as the diameter of a sphere or a rod), the lattice constants (the shortest distances over which the structure repeats), and the number of layers. The condition that these characteristic lengths be comparable to the wavelength dictates the operational frequency range of the phononic crystal, which can thus be tuned from hundreds of hertz to gigahertz.

Since about 1990, there has been a growing number of theoretical and experimental studies of phononic crystals, illustrating the wide range of different phononic materials that can be constructed and allowing their remarkable properties to be investigated. Phononic crystals can be used to block sound propagation over certain frequency ranges due to the formation of band gaps, and can cause sound to bend in unusual ways (negative refraction) at other frequencies, leading to a new way of focusing sound using a material with flat surfaces.

Band gaps. One of the main features of phononic crystals that distinguishes them from uniform materials is the existence of the frequency ranges, known as band gaps, in which acoustic waves cannot propagate. The basic physics explaining the existence of these acoustic band gaps is similar to the band theory of solids, which explains the formation of energy bands and band gaps for electrons in metals, semiconductors, and insulators. In atomic crystals, the Bragg scattering of the electron wavefunctions (brought about by the periodic arrangement of the atoms) makes them interfere destructively at certain energies, effectively creating ranges of energy (band gaps) for which no electron states exist. The same Bragg scattering of acoustic waves inside phononic crystals is responsible for the creation of frequency band gaps, with the result that no propagating modes exist at such frequencies. When the gap exists in all directions, it is called a complete band gap, while if there are no modes only in certain directions, the term stop band is used.

The effects of periodic structure on wave propagation are most conveniently represented by a band structure plot, where the frequency is plotted as a function of wave vector along different crystal directions (**Fig. 1***a*). The example shown depicts the

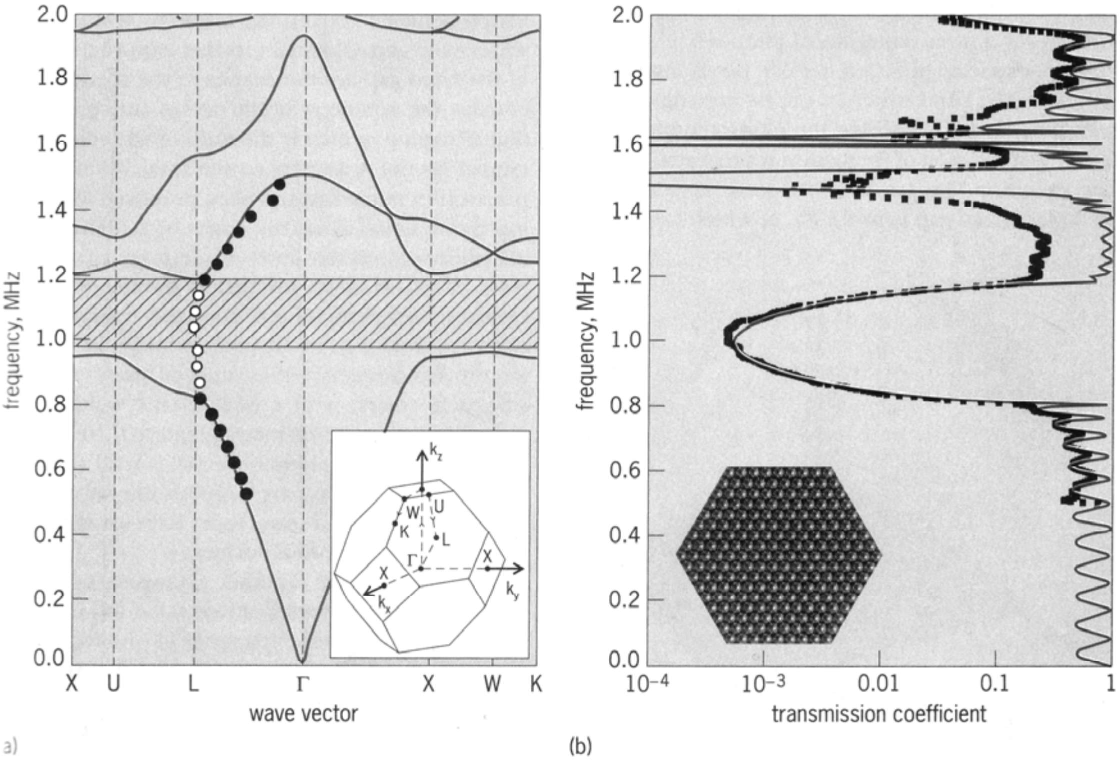

Fig. 1. Band structure and transmission coefficient of a face-centered-cubic phononic crystal of tungsten carbide beads in water. (*a*) Band structure plot. Solid curves give the variation of the frequency with the wave vector along high-symmetry directions of the crystal, as calculated using multiple scattering theory. The different crystallographic directions of the wave vector are represented by the capital letters explained in the inset. Data points give representative experimental results obtained from ultrasonic phase velocity experiments on a 12-layer crystal; solid and open symbols correspond to measurements in the pass and stop bands, respectively. (*b*) Frequency dependence of the ultrasonic transmission coefficient through this 12-layer phononic crystal for waves traveling parallel to a body diagonal of the cubic unit cell. Solid curves give results of multiple scattering theory; data points give experimental results. The inset shows a top view of the crystal.

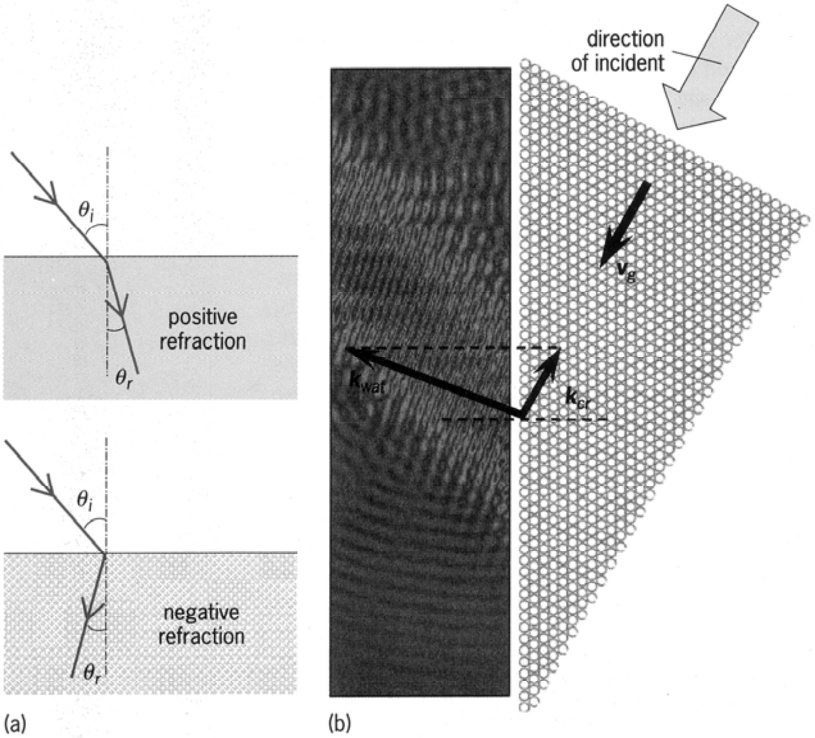

Fig. 2. Phenomenon of negative refraction. (*a*) Comparison of positive and negative refraction at an interface. θ_i = angle of incidence; θ_r = angle of refraction. (*b*) Negative refraction of ultrasonic waves emerging from a 2D phononic crystal prism. The directions of the group velocity, v_g, and of the wave vector, k_{cr}, inside the crystal, and of the wave vector in the water, k_{wat}, are shown by arrows.

band structure, calculated using multiple scattering theory, for a three-dimensional phononic crystal of 0.8-mm-diameter tungsten carbide beads immersed in water. The band structure can be investigated experimentally by measuring the ultrasonic phase velocity as a function of frequency; representative data are shown in Fig. 1*a*. This phononic crystal has a complete band gap near 1 MHz, at which frequency the spacing between adjacent planes of beads is approximately half the ultrasonic wavelength in water. For the frequencies in the band gap, the transmission coefficient or fraction of the incident wave amplitude that is transmitted through the crystal exhibits a deep minimum (Fig. 1*b*).

However, in a band gap the transmitted signal is not zero, although there are no propagating modes. The origin of this signal is explained by the tunneling of ultrasound, an effect that is completely analogous to the tunneling of a quantum-mechanical particle through a potential barrier. As a result, the transmission coefficient decreases exponentially with crystal thickness in a band gap, and is thus very small even for thin crystals. A remarkable signature of the tunneling mechanism is that the velocity of a pulse transmitted through the crystal (the group velocity) can be larger that in any of the constituent materials, and increases with the crystal thickness. This unusual effect has been observed experimentally using ultrasonic waves, in good agreement with theoretical predictions.

Application to noise suppression. Because of the ability of phononic crystals to effectively block sound waves over a range of frequencies, they can be used as acoustic filters, suppressing noise in places where a vibrationless or noise-free environment is desired. Consequently, it is of the great importance to determine and optimize the factors that influence the width of the band gap. In general, for two phononic crystals having the same crystal structure, the one with the greater density and sound velocity mismatch between constituent materials will have the wider band gap. Other factors that control the width of the band gap are the shapes of the scattering elements, the symmetry of the crystal lattice, and the filling fraction, which is the ratio of the volume occupied by the scatterers to the total volume. One practical example that has been proposed for blocking traffic noise along the edges of a highway is a 2D phononic crystal fence made from an array of solid cylinders in air. Another is the use of locally resonant microstructures to construct compact crystals with band gaps in the audible range. By exploiting the low-frequency resonance of heavy spherical scatterers coated with a weak elastic material and embedded in a stiffer matrix material, band gaps can be obtained in phononic crystals with interscatterer separations that are 1/100th the wavelength in air. Such compact structures have considerable potential for noise-proof devices.

Applications of defects. Another promising field with numerous potential applications takes advantage of defects to modify wave transport in phononic crystals. Defects may be any objects breaking the symmetry in the otherwise perfect crystal. For example, in case of a two-dimensional phononic crystal, the defect can be a single rod that differs in its acoustic properties from the rest of the rods (for example, the defect rod may be hollow, of different shape, or made of different material) or simply a missing rod. It has been shown both theoretically and experimentally that, as a result of such modifications,

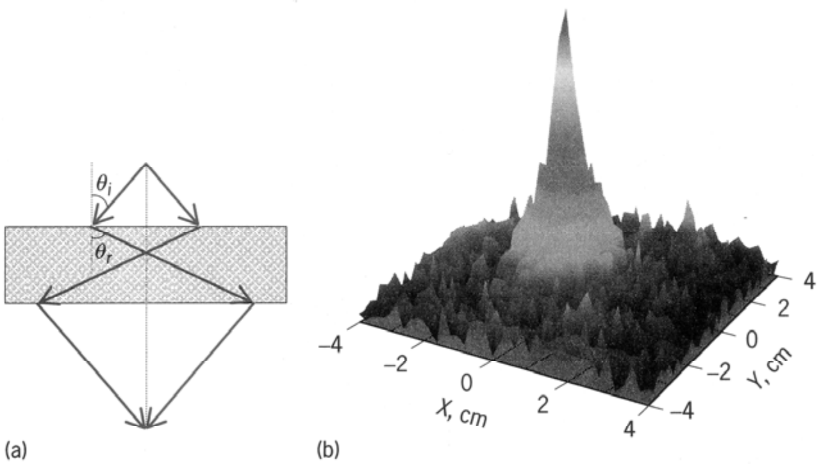

Fig. 3. Focusing by negative refraction. (*a*) Ray diagram showing how a point source may be focused by negative refraction in a phononic crystal. (*b*) Demonstration of focusing by negative refraction in a 3D phononic crystal; this picture shows the focal spot obtained when a diverging beam from a small-diameter transducer is imaged by the crystal. The height of the surface maps the sound intensity across the neighborhood of the focal point. (*After S. Yang et al., Focusing of sound in a 3D phononic crystal, Phys. Rev. Lett., 93:024301:1–4, 2004*)

the transmission spectrum of the phononic crystal with the defect exhibits a narrow peak at a particular frequency inside the band gap. By changing the different characteristics of the defect (for example, changing the inner or outer diameters of a hollow rod or filling the rod with various fluids), the frequency of the transmitted peak can be controlled. Thus, phononic crystals with defects may be used as tunable acoustic filters to select waves of a certain frequency.

By removing an entire row of rods, a line defect inside a 2D phononic crystal can be created. If the crystal has a complete band gap, waves entering the line defect will be confined inside it, creating a waveguide for acoustic waves. The waveguide also can be made tunable to transmit waves of a selected frequency or frequencies. To this end, the line defect can be created by using rods different from the rest of the rods in the phononic crystal rather than removing the rods completely. These applications of defects in 2D crystals can be readily extended to 3D phononic crystals, even though their implementation may be more difficult to engineer.

Negative refraction and sound focusing. Another unusual phenomenon exhibited by phononic crystals is negative refraction. At some frequencies, ultrasonic waves entering or leaving a phononic crystal may bend in a direction that is opposite to the norm for uniform materials, so that the effective angle of refraction at the interface is negative (**Fig. 2*a***). This effect can occur when the group velocity, $\boldsymbol{v}_g$, which determines the direction in which energy is transported through the crystal (and hence the ray direction), points in a different direction than the wave vector, $\boldsymbol{k}$, which describes the direction of travel of the phase oscillations in the wave. In the simplest case of negative refraction, $\boldsymbol{v}_g$ and $\boldsymbol{k}$ are antiparallel.

Figure 2*b* shows an example of negative refraction for ultrasonic waves emerging from a prism-shaped phononic crystal of steel rods in water. The waves are incident from the upper right side of the figure. The directions of the group velocity, $\boldsymbol{v}_g$, and of the wave vector inside the crystal, $\boldsymbol{k}_{cr}$, are shown by arrows. In this frequency range, which corresponds to the second pass band of the crystal, the frequencies of the modes decrease as the wave vector increases (similar to the branches of the 3D band structure shown in Fig. 1*a* for frequencies above 1.2 MHz); hence the group velocity $\boldsymbol{v}_g$, which is given by the derivative of frequency ω with respect to wave vector, has the opposite sign to the wave vector. Since the wave can be transported across the crystal only when the group velocity is positive, the wave vector $\boldsymbol{k}_{cr}$ points backward, as indicated. (In general, the relationship between the direction of the group velocity and the wave vector can be found by determining the equifrequency or slowness surface, which displays the magnitude of the wave vector as a function of its direction for waves of a single frequency. Since $\boldsymbol{v}_g = \nabla_{\boldsymbol{k}}\omega(\boldsymbol{k})$, $\boldsymbol{v}_g$ is perpendicular to this surface; it points in the opposite direction to $\boldsymbol{k}$ if the equifrequency surface is circular and if the surface shrinks in size as frequency increases, as is the case here.) Consequently, Snell's law, which states that the component of the wave vector parallel to the interface should be the same on both sides of the boundary, predicts that a negatively refracted wave will emerge from the prism crystal as shown. These experimental results are in excellent agreement with predictions based on multiple scattering theory for the magnitudes and directions of the wave vector and the group velocity for this 2D crystal.

The ability of phononic crystals to refract sound waves negatively allows them to be used as lenses for focusing sound. When an initially diverging beam from a source point is incident on the crystal, the rays are bent back by negative refraction toward the axis of the lens, so that when they emerge of the far side of the crystal, where they travel in their original directions, they are brought to a focus (**Fig. 3*a***). The focusing of sound by a flat 3D phononic crystal has been demonstrated experimentally (Fig. 3*b*). A potential advantage of this novel type of focusing is improved resolution compared with traditional lenses, and theoretical predictions of image of a point source as small as one-seventh the wavelength have been made.

For background information *see* ACOUSTIC NOISE; BAND THEORY OF SOLIDS; COMPOSITE MATERIAL; CRYSTAL DEFECTS; GROUP VELOCITY; REFRACTION OF WAVES; SOLID-STATE PHYSICS; TUNNELING IN SOLIDS in the McGraw-Hill Encyclopedia of Science & Technology.

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Phylogenetic diversity and conservation

"Biodiversity" refers to the variety of life on the planet—extending in scale from genes to species to ecosystems. Our understanding of biodiversity conservation, however, faces a twofold knowledge gap. First, we have no complete list of the components of biodiversity at the different levels, and second, it is difficult to judge what their values might be in the future. Therefore a core strategy for biodiversity conservation is to estimate patterns of variation, and then try to conserve as much of that variation as possible, so as to retain the full range of possible future values.

Phylogeny, the evolutionary "tree of life," can play an important role in estimating biodiversity patterns. A phylogenetic pattern for a taxonomic group displays evolutionary relationships among species, or