

379 The Châtelperronian technologies of the French
380 Neanderthals would seem to reflect a change in
381 lifestyle, but the rate of change was too fast to allow
382 their bodies to change.

383 Instead, a population of moderns with a more
384 gracile build, which has been shown recently to
385 have been expert at endurance running, reached the
386 steppes and plains of central Asia and eastern Europe
387 where it encountered an untapped larder of large
388 mammals, from woolly mammoth to steppe bison,
389 living in treeless landscapes. These people devel-
390 oped portable tool kits and projectile technology. In
391 a world of expanding treeless landscapes, these mod-
392 erns found a door that led them west into Europe and
393 east toward Siberia and, eventually, North America.

394 Meanwhile, Neanderthals were managing to sur-
395 vive in their classic landscapes of semi-open veg-
396 etation with scattered woods and bushland. These
397 were restricted to the south and west where climate
398 was less severe. It is here that the last populations
399 held out, but their numbers were so low that extinc-
400 tion was inevitable. The most recent evidence has
401 revealed that the last populations living in Gibraltar
402 were hit badly by a series of harsh climatic events
403 in which drought seems to have been a key factor
404 causing their disappearance.

405 Rather than seeking a single cause to the Nean-
406 derthal extinction, however, we should see the pro-
407 cess as a protracted one that lasted tens of thousands
408 of years. The last populations in Gibraltar went ex-
409 tinct because of local climatic effects, but it is equally
410 plausible that others disappeared because of inbreed-
411 ing, disease, or localized competition from other hu-
412 mans.

413 For background information see EARLY MODERN
414 HUMANS; EXTINCTION (BIOLOGY); FOSSIL HUMANS;
415 MOLECULAR ANTHROPOLOGY; NEANDERTALS; PALEO-
416 CLIMATOLOGY; PHYSICAL ANTHROPOLOGY; PREHIS-
417 TORIC TECHNOLOGY in the McGraw-Hill Encyclope-
418 dia of Science & Technology. Clive Finlayson

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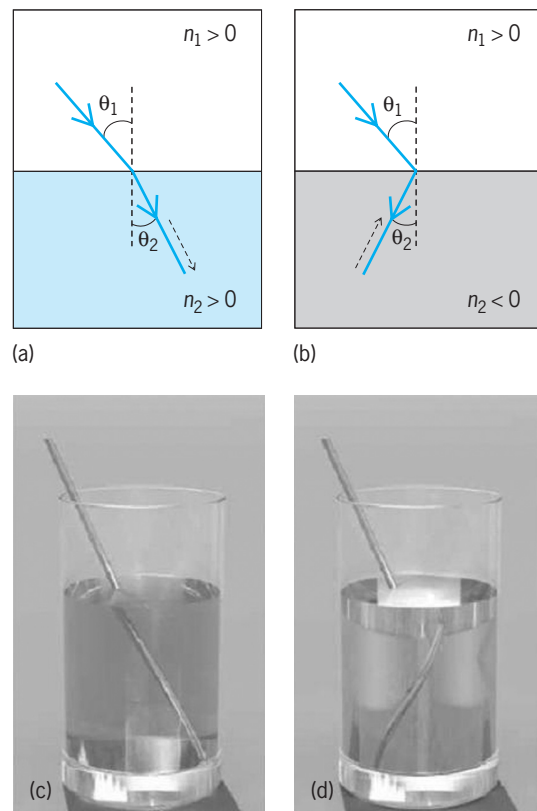
437 Negative refraction

438 Refraction is one of the most fundamental phenom-
439 ena in nature. It gives rise to such well-known ef-
440 fects as the apparent bending of objects partly im-
441 mersed in water, rainbows, mirages, green flashes,

442 and haloes. Refraction is also utilized in many ex-
443 isting optical instruments, including microscopes,
444 telescopes, and eyeglasses. All these phenomena and
445 applications rely on conventional or “positive” re-
446 fraction. What would the world look like if the sign
447 of refraction were reversed?

448 The law of refraction predicts that an electromag-
449 netic wave, crossing the interface between two ma-
450 terials with refractive indices n_1 and n_2 , changes its
451 trajectory, depending on the difference in the refrac-
452 tive indices, such that $n_1 \sin \theta_1 = n_2 \sin \theta_2$, where θ_1
453 and θ_2 are the angles from the normal of the incident
454 and refracted waves. The direction of the refracted
455 wave depends on the sign of n_2 (assuming $n_1 > 0$).
456 The refraction is referred to as positive when $n_2 > 0$
457 (Fig. 1a) and as negative when $n_2 < 0$ (Fig. 1b). While
458 positive refraction is a well-known phenomenon, a
459 negative index of refraction leads to many unusual
460 and often surprising effects. For example, Fig. 1c and
461 d show calculated images of a metal rod in a glass
462 filled with regular water and in a glass filled with
463 negative-index water.

464 **Left-handed world.** The refractive index is one of
465 the basic characteristics of electromagnetic wave
466 propagation in continuous media. It is closely related
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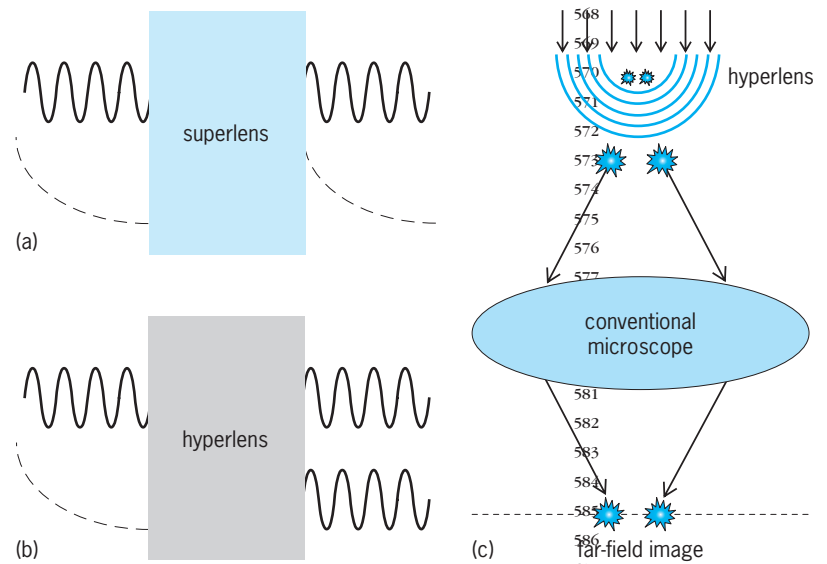
505 **Fig. 1. Refraction: Diagrams of (a) positive refraction and (b) negative refraction; and calculated images of a metal rod (c) in a glass filled with regular water ($n = 1.3$), and (d) in a glass filled with “negative-index water” ($n = -1.3$). In parts a and b, solid lines with arrows indicate the direction of the energy flows, broken lines with arrows show the direction of the wave vectors. (Parts c and d from G. Dolling et al., Photorealistic images of objects in effective negative-index materials, *Opt. Express*, 14:1842-1849, 2006)**

505 to two fundamental physical parameters that charac-
 506 terize material properties, the dielectric permittivity
 507 ϵ and the magnetic permeability μ , through the equa-
 508 tion $n = \pm\sqrt{\epsilon\mu}$. While nearly all transparent conven-
 509 tional materials have positive ϵ and μ , correspond-
 510 ing to positive n , there are no fundamental physical
 511 reasons prohibiting materials from possessing simul-
 512 taneously negative ϵ and μ , and as a result negative
 513 n . Although not found in nature, such materials were
 514 recently created artificially and were named “meta-
 515 materials.”

516 A detailed theoretical study of electromagnetic
 517 wave propagation in materials with simultaneously
 518 negative ϵ and μ was performed by Victor Veselago
 519 in 1967. Maxwell’s equations, which relate the elec-
 520 tric field E , the magnetic field H , and the wave vector
 521 k , predict that E , H , and k form a “left-handed” set
 522 and the sign of the refractive index is negative if both
 523 ϵ and μ are negative, and a “right-handed” set if both
 524 ϵ and μ are positive. The former class of materials is
 525 often referred to as left-handed materials or negative-
 526 index materials (NIMs), while the latter class is re-
 527 ferred to as right-handed materials or positive-index
 528 materials (PIMs). At the same time, the direction of
 529 the Poynting vector S , which defines the direction
 530 of the energy flow, is the same in positive-index and
 531 negative-index materials. Thus, the Poynting vector
 532 is antiparallel to the k -vector in negative-index ma-
 533 terials and is parallel to the k -vector in positive-index
 534 materials. The opposite directionality of the k -vector
 535 and the Poynting vector is often taken as the most
 536 general definition of negative-index materials. There-
 537 fore, the negative refraction illustrated in Fig. 1 is a
 538 direct result of the opposite directionality of k and S
 539 and of the continuity of the tangential components
 540 of the wave vector at the interface between the two
 541 media.

542 Although the term “left-handed materials” was
 543 originally coined to describe materials with simul-
 544 taneously negative ϵ , μ , and n , currently it is used
 545 in a broader context to include other optical struc-
 546 tures that possess antiparallel k -vectors and Poynting
 547 vectors and support negative refraction. Examples of
 548 such materials include photonic crystals, anisotropic
 549 waveguides, organic and uniaxial gyrotropic crystals
 550 and a thin film on a metal substrate, and nanotrans-
 551 mission lines.

552 Negative refraction has been demonstrated at mi-
 553 crowave frequencies in a metamaterial wedge and in
 554 the visible frequency range at the interface between
 555 a bimetal Au-Si₃N₄-Ag waveguide and a conventional
 556 Ag-Si₃N₄-Ag slot waveguide using plasmons. Negative
 557 refraction at optical frequencies was demonstrated in
 558 photonic crystals. Although many unusual phenom-
 559 ena associated with the negative index of refraction
 560 can be observed in photonic crystals, the main limita-
 561 tion of photonic crystals is that the size of their char-
 562 acteristic features is comparable to the wavelength of
 563 light. On the contrary, optical metamaterials with fea-
 564 ture sizes much smaller than the wavelength of light
 565 are predicted to enable many truly remarkable phe-
 566 nomena. However, currently optical metamaterials
 567 are available only in the form of subwavelength thin



588 **Fig. 2. Schematics of (a) superlens, (b) hyperlens, and (c) imaging system using a**
 589 **hyperlens. In parts a and b, solid lines correspond to the propagating field components,**
 590 **broken lines correspond to the evanescent field components.**

591 films, thus permitting the measurement of a phase
 592 advance but not of negative refraction per se.

593 Besides negative refraction, negative-index materi-
 594 als have been predicted to give rise to a wide vari-
 595 ety of extraordinary linear and nonlinear optical phe-
 596 nomena, including reversed Cerenkov radiation, the
 597 reversed Doppler effect, backward phase-matched
 598 second-harmonic generation and optical parametric
 599 amplification, lasing without a cavity, bistability, and
 600 gap solitons in PIM-NIM couplers with no external
 601 feedback.

602 **Superresolution: from “super” to “hyper” lens.** A
 603 very unusual property of negative-index materials
 604 gives rise to the possibility of imaging using a flat
 605 slab of negative-index material with $n = -1$ sur-
 606 rounded by a conventional medium with $n = 1$.
 607 Moreover, under the appropriate conditions this
 608 slab not only focuses propagating field components
 609 but also recovers the evanescent field components,
 610 which decay exponentially with distance from the
 611 source (Fig. 2a), through the excitation of a plas-
 612 mon resonance on the surfaces of the negative-index
 613 material. These evanescent field components, which
 614 are responsible for imaging of the high-frequency
 615 and correspondingly small-scale features of the ob-
 616 ject, cannot be restored by conventional lenses, in-
 617 evitably limiting their resolution. Thus, at least in
 618 the ideal (lossless) case, an imaging system based
 619 on a slab of negative-index material, named a “super-
 620 lens” by John B. Pendry, has the potential for signifi-
 621 cantly improving resolution in the image plane. Unfor-
 622 tunately, a superlensing effect is extremely sensitive
 623 to losses in the negative-index-material slab. While
 624 the superlens is likely to be useful in numerous near-
 625 field applications, including biomedical imaging and
 626 nanolithography, superresolution in the far field is
 627 challenging.

628 Recently, a promising solution, a hyperlens, was
 629 proposed independently by Nader Engheta and
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631 Evgenii Narimanov. Instead of reamplifying and refo-
 632 cusing the evanescent field components as Pendry's
 633 superlens does, a hyperlens converts those evanes-
 634 cent waves into propagating waves (Fig. 2*b*). Once
 635 all the components are propagating waves, they
 636 can easily be imaged by a conventional lens (micro-
 637 scope) in the far field (Fig. 2*c*). The only remain-
 638 ing limitation of a hyperlens is that the object
 639 plane must be situated very close to the hyperlens
 640 surface.

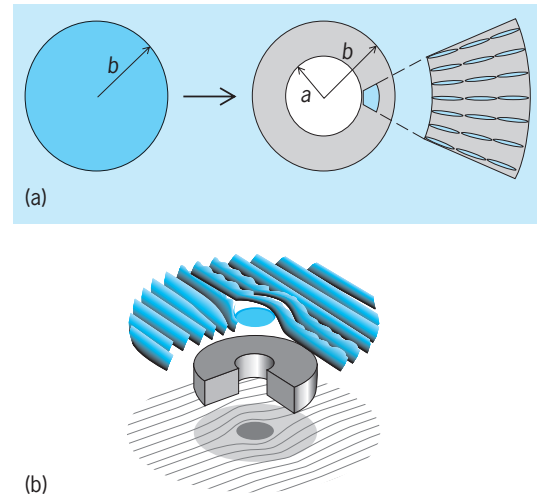
641 **Optical metamaterials.** Many of the predicted ex-
 642 traordinary properties of negative-index materials
 643 would not have been possible without rapid progress
 644 in the design and fabrication of optical metamate-
 645 rials. As mentioned above, no materials in nature
 646 possess negative ϵ and μ in the same range of fre-
 647 quencies. While dielectric permittivity of some ex-
 648 isting materials is negative at certain frequencies, no
 649 isotropic materials with negative μ are known. More-
 650 over, magnetism is usually weak at optical frequen-
 651 cies so that $\mu \approx 1$.

652 On the contrary, metamaterials are built of artificial
 653 or "meta" atoms, which are resonant structures such
 654 as split-ring resonators and paired metal nanorods or
 655 nanostrips. The meta-atoms can be engineered and
 656 arranged such that their ϵ , μ , and n are positive, nega-
 657 tive, or even zero at any selected frequency. The first
 658 optical metamaterials with a negative index of refraction
 659 have been demonstrated using paired nanorods,
 660 and independently by another group using paired die-
 661 lectric voids in metal.

662 While these first experiments confirmed the possi-
 663 bility of the realization of a negative index of refraction
 664 at optical frequencies, the negative-index materi-
 665 als were realized only in the form of subwavelength
 666 films and possessed significant losses. Some essential
 667 requirements for practical negative-index-material
 668 designs include minimized losses or a large ratio of
 669 the real and imaginary parts of n , often taken as a fig-
 670 ure of merit; a broad bandwidth over which both ϵ
 671 and μ are negative; optimized impedance matching;
 672 and realization of three-dimensional negative-index
 673 materials.

674 Using a self-supporting fishnet structure consisting
 675 of rectangular dielectric voids in parallel metal films,
 676 a figure of merit of 3 has been demonstrated at a
 677 wavelength $\lambda = 1.4 \mu\text{m}$. This structure represents
 678 the current state-of-the-art for optical negative-index
 679 materials. Recently, the first three-layered negative-
 680 index material with a figure of merit of 2.5 at $\lambda =$
 681 $1.41 \mu\text{m}$ was also reported.

682 **Refractive index engineering.** While one of the origi-
 683 nal motivations behind the development of meta-
 684 materials was the demonstration of negative-index
 685 materials, metamaterial technology has stimulated
 686 rapid progress in an entirely new and exciting branch
 687 of modern optics, transformation optics, which is
 688 based on the idea of mapping a coordinate transfor-
 689 mation to a set of material parameters, ϵ and μ .
 690 Metamaterials allow precise control over these ma-
 691 terial parameters and, more generally, enable refrac-
 692 tive index engineering. Such mapping turned out to
 693 be particularly useful for cloaking applications and



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712 **Fig. 3. Cloaking. (a) The transformation of a cylindrical**
 713 **region $r < b$ into a concentric cylindrical shell $a < r < b$ and**
 714 **an enlarged section of a nonmagnetic optical cloak built**
 715 **with metal wires embedded in a dielectric host. (b) Numerical simulations of an ideal metallic cylinder with**
 716 **radius $r = a$ illuminated with TM (transverse-magnetic)-**
 717 **polarized wave with the cloak turned "on."**

718 facilitated the first experimental demonstration of
 719 cloaking of a copper cylinder at microwave frequen-
 720 cies. In that experiment the object was concealed
 721 by a cylindrical metamaterial cloak built using split-
 722 ring resonators. The coordinate transformation and
 723 a schematic of the first nonmagnetic cloak operat-
 724 ing at optical frequencies, as proposed theoretically,
 725 are illustrated in Fig. 3*a*. Figure 3*b* shows the re-
 726 sults of numerical simulations of cloaking of an ideal
 727 metallic cylinder. Currently, in both microwave and
 728 optical cloak designs, the effect has been achieved at
 729 only one frequency. Obviously, broadband cloaking
 730 would be desirable for most practical applications,
 731 and further research is therefore required.

732 Finally, cloaking is only one realization of the great
 733 potential of transformation optics in conjunction
 734 with metamaterials. Other promising applications
 735 include field concentrators and a variety of reflec-
 736 tionless devices. Metamaterials are bringing new de-
 737 grees of freedom for designing structures with almost
 738 any desired optical properties, thus presenting enor-
 739 mous opportunities for a wide range of applications
 740 relying on refractive index engineering.

741 For background information see MAGNETISM;
 742 MAXWELL'S EQUATIONS; PERMITTIVITY; PLASMON;
 743 POYNTING'S VECTOR; REFRACTION OF WAVES in the
 744 McGraw-Hill Encyclopedia of Science & Technology.

745 [The authors gratefully acknowledge the sup-
 746 port of the Army Research Office through Grants
 747 W911NF-07-1-0343 and 50342-PH-MUR.]

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763 New coatings for wood

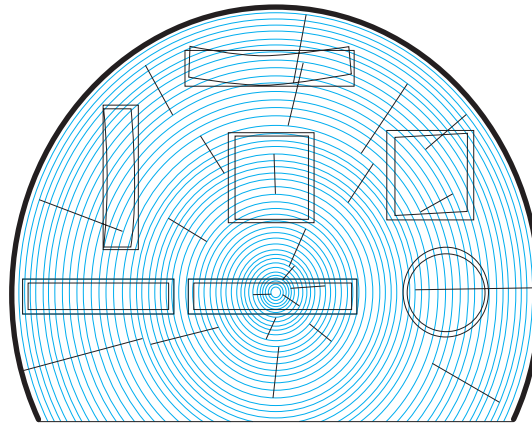
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 765 There has never been a broader array of coatings
 766 for wood available on the market than now. In the
 767 past, coatings for wood, such as stains, primers,
 768 and top coats, were primarily oil-based. However,
 769 as new air-quality regulations have mandated lower
 770 volatile organic content (VOC) in architectural coat-
 771 ings throughout the United States and now proposed
 772 in Canada, manufacturers have had to reformulate
 773 their products to meet the new regulations. [Volatile
 774 organic compounds are organic chemicals that pro-
 775 duce vapors readily at room temperature and normal
 776 atmospheric pressure, including gasoline and sol-
 777 vents such as toluene, xylene, and tetrachloroethy-
 778 lene, which form photochemical oxidants (including
 779 ground-level ozone) that affect health, damage mat-
 780 erials, and cause crop and forest losses; many are also
 781 hazardous air pollutants.]

782 There are two primary approaches to reformulat-
 783 ing a low-VOC coating for wood. In the majority of
 784 these reformulations, the solvent portion of the prod-
 785 uct has been replaced with water. In a smaller per-
 786 centage of these reformulations, the amount of solid
 787 ingredients has increased significantly to produce a
 788 high-solids coating. Given the special characteristics
 789 of wood, each of these approaches has presented
 790 challenges to the coatings formulator and, ultimately,
 791 the user of these coatings.

792 **Characteristics of wood.** Wood is one of the world's
 793 most common materials of construction. As such, it
 794 is a renewable resource, easy to use, and durable for
 795 centuries when properly maintained. It can come
 796 from hardwood, softwood, or tropical wood species.
 797 However, regardless of origin, once the tree is har-
 798 vested from the forest, it becomes vulnerable to at-
 799 tack by a host of enemies. Degradation can come
 800 from water, sunlight, insects, and microorganisms.

801 By far, water is wood's worst enemy. Because
 802 wood comprises about 50% cellulose and 25% hemi-
 803 cellulose, it is subject to swelling and shrinking as it
 804 gets wet and dries. Continued wet/dry cycles create
 805 a continuous movement of wood that causes stress
 806 between the wet surface and the dry interior. This
 807 stress causes cracking, warping, bowing, twisting,
 808 and cupping of wood, resulting in structural prob-
 809 lems. This excessive moisture also invites microor-
 810 ganisms such as mold and mildew to grow, causing
 811 aesthetic problems. Continued exposure to moisture
 812 will lead to rot and destruction of the wood itself.

813 Thus, understanding the characteristics of wood
 814 is critically important for the coatings formulator.
 815 The very nature of wood's reaction to water is what
 816 makes an oil-based coating an easier product to use
 817 on wood and a water-based coating more difficult
 818 to use on wood. When water-based coatings are ap-
 819 plied to wood, they will usually swell the grain of



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Fig. 1. Mixed grain patterns cause differences within wood that result in cupping and warping. Where the wood is cut from the tree determines how the wood will warp when exposed to water. (From Wood Handbook: Wood as an Engineering Material, USDA Forest Service)

the wood, causing grain raising (**Fig. 1**). This usually results in the need for sanding, especially on fine furniture and cabinetry. Because they tend to dry faster as the water soaks into the wood, water-based stains are subject to lapping, which is seen as a darker area at the overlap of two brush strokes applied side by side. Other problems can occur in exterior water-based coatings for wood such as poor water resistance and adhesion failure compared to oil-based coatings. In order to understand why these problems occur, it is necessary to know the basics of how water-based coatings are formulated and how they differ from their oil-based counterparts.

Conventional oil-based coatings. Conventional oil-based coatings usually have several basic categories of ingredients that can be broken down into four main groups: solvent, binder, pigments/fillers, and driers/additives. The solvent acts as a carrier for the other ingredients and usually comprises one or more petroleum distillates such as mineral spirits, mineral oil, or xylene. It is this component of oil-based coatings that contributes to the depletion of the atmospheric ozone layer, and its content is now regulated by governmental agencies.

Binders can be as simple as drying oils such as linseed, tung, teak, or soybean oil or more highly formulated chemicals such as alkyds (a class of adhesive resins made from unsaturated acids and glycerol), polyurethane, epoxies, silicones, and fluorinated polymers. These generally deliver the bulk of the protection properties to the wood. Binders can be used by themselves or in combination.

Pigments and fillers impart color and opacity to a coating. Pigments generally are composed of iron oxides that result in basic brown, red, and yellow tones, but they can be as sophisticated as highly formulated organic molecules that impart stronger, intense colors like deep greens, reds, and blues. The most common white pigment is titanium dioxide. Fillers are usually made up of mined materials such as clay, calcium carbonate, mica, talc, or diatomaceous earth (yellow, white, or light-gray, siliceous, porous deposit made of the opaline shells of diatoms). They