other domains (twins) have different azimuthal orientations. Figure 3D shows a high-resolution structure image of a thin area of grain “M,” showing a good correspondence to the inserted structure model.

Ferroelectric polarization–electric field (P-E) hysteresis loops and simultaneously recorded displacement currents of BLT films (thickness 1 μm) with α_{110} = 99% were recorded at 200 Hz, as shown in Fig. 4A. Platinum top electrodes (diameter 100 μm) were sputter-deposited. The films revealed well-saturated hysteresis loops (Fig. 4A) with a remanent polarization of our films im-
plies that there are almost no a-b twins present or that the latter are totally switched into the a-axis orientation.

Although this high growth temperature most proba-
ably does not comply with memory device fabrication, it can probably be reduced by using other oxidants instead of O₂, including nitrous oxide (N₂O) or nitro-
gen dioxide (NO₂) (29, 30).

18. In this paper, a-b growth twins are not explicitly considered. The difference between the lattice pa-
tameters a and b of BLT is so small that it is difficult to discriminate between them. However, the high value of the remanent polarization of our films im-
plies that there are almost no a-b twins present or that the latter are totally switched into the a-axis orientation.
20. It is now possible to implement control strategies that yield new modes of spatio-
temporal behavior in excitable chemical and biological media. Feedback methods that yield particle-like waves in this system by thermally altering local cat-
alytic efficiencies, and focused laser light have been used to direct wave propagation in a chemical reaction-
diffusion system with spatiotemporal feedback. Wave behavior is controlled by feedback-regulated excitability gradients that guide propagation in specified directions. Waves interacting with boundaries and with other waves are ob-
served when interaction terms are incorporated into the control algorithm. Spatiotemporal feedback offers wide flexibility for designing and controlling wave behavior in excitable media.

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Design and Control of Wave Propagation Patterns in Excitable Media
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Intricate patterns of wave propagation are exhibited in a chemical reaction-
diffusion system with spatiotemporal feedback. Wave behavior is controlled by feedback-regulated excitability gradients that guide propagation in specified directions. Waves interacting with boundaries and with other waves are ob-
served when interaction terms are incorporated into the control algorithm. Spatiotemporal feedback offers wide flexibility for designing and controlling wave behavior in excitable media.
waves is controlled by imposing excitability gradients that are regulated by a secondary feedback loop. We present experimental realizations and numerical simulations that demonstrate unprecedented control of spatiotemporal wave activity.

We carried out experiments using a photosensitive BZ medium that was monitored with a video camera and illuminated with a computer-controlled video projector. A thin layer of silica gel (0.3 mm × 20 mm × 30 mm) containing immobilized ruthenium(II)bipyridyl, a light-sensitive catalyst for the BZ reaction, was cast onto a microscope slide. This gel was bathed in continually refreshed catalyst-free solution so that a particular non-equilibrium state could be maintained for study (12, 13).

Images of the waves were captured with a video camera and processed by a computer in real time to return control images to the gel via the video projector. The excitability of the medium is determined by the photochemical production of bromide ion (14, 15), and, hence, a desired excitability at each pixel could be imposed by the illumination intensity (16). A new illumination pattern was calculated for every iteration, according to the following control algorithm:

\[ \phi(x, y) = aA + b + cG(x, y) \]
\[ A = \sum_{x,y} \Theta [p(x, y) - p_m] \]

where \( \phi(x, y) \) is the output image to the projector and \( p(x, y) \) is the input image from the video camera. The wave area (A) is defined as the region containing the oxidized ruthenium catalyst \([\text{Ru(bpy)}_3^{2+}]\) and is obtained by counting the video image pixels with a gray level \( p(x, y) \) above the threshold \( p_m \), where \( \Theta \) is the Heaviside function giving 0 or 1 in the summation (12). The gain \( a \) and offset \( b \) define the primary feedback loop, which increases or decreases the excitability of the medium as the wave becomes smaller or larger, respectively, thus stabilizing the wave size. The term \( G(x, y) \), with gain \( c \), represents the small variation in light intensity imposed to direct the motion of the wave according to a secondary feedback loop, different implementations of which are presented below. Two or more waves can be independently controlled, each with its own feedback loop, by localizing the feedback around each wave.

Different realizations of \( G \) give rise to different patterns of wave motion. In the simple case of a radially symmetrical distribution, \( G(r) = \ln(r) - \ln(r_0) \), the motion of a wave resembles that of a particle in a potential field (17). To minimize the effect of directional control on the wave size, the second term, \( \ln(r_0) \), maintains \( G = 0 \) at the wave "center of mass." Figure 1 shows the trajectories of three experimental waves, where the initial wave position was slightly varied with respect to the center of the symmetrical gradient. Also shown are three wave trajectories simulated with the Oregonator model for the photosensitive BZ reaction (18–21). The trajectories in both the experiments and simulations would be horizontal in a gradient-free field; however, each is increasingly deflected by the "attracting field." The most highly curved trajectories in Fig. 1, A and B, closely approach the center of the symmetrical gradient.

Much greater flexibility for realizing complex wave trajectories is possible when \( G \) is dynamically varied according to the current and target locations of the wave. The direction of wave propagation can be conveniently controlled by using a simple linear gradient applied perpendicular to the direction of propagation at the wave center of mass (12). The wave turns to the left or right, depending on the sign of the gradient, and at a rate that depends on its magnitude. Figure 2 shows examples of wave trajectories in which the gradient is proportional to the deviation of the wave position from a hypotrochoidal path \((X, Y)\) computed according to:

\[ X = (\alpha - \beta \cos(\theta)) + \gamma \cos \left( \frac{\alpha - 1}{\beta} \theta \right) \]
\[ Y = (\alpha - \beta \sin(\theta)) - \gamma \sin \left( \frac{\alpha - 1}{\beta} \theta \right) \]

Fig. 1. Wave trajectories in a radially symmetrical excitability distribution defined by \( G(r) = \ln(r) - \ln(r_0) \) in Eq. 1, where \( r \) is the radial coordinate and \( r_0 \) is the distance between the center of the distribution and the center of mass of the wave. (A) A superposition of snapshots taken every 40.0 s of experimental wave behavior. (B) A superposition of snapshots taken every 0.1 dimensionless time units of simulated wave behavior. The values of \( \phi \) in Eq. 1 were bounded by the minimum and maximum intensities of the video projector, and analogous bounds were included in the simulations. The feedback parameters \( a \) and \( b \), and the directional gain \( c \), were 0.55, 35.0, and 120.0 in the experiments and 0.304, −5.10, and 0.025 in the simulations. The scale bar in (A) is 2.0 mm.

Fig. 2. Hypotrochoidal trajectories resulting from controlling wave propagation according to Eqs. 1 and 2. (A, C, and E) A superposition of snapshots taken every 0.1 dimensionless time units of simulated wave behavior. (B, D, and F) A superposition of snapshots taken every 40.0 s of experimental wave behavior. (B, D, and F) A superposition of snapshots taken every 0.1 dimensionless time units of simulated wave behavior. The target trajectories (solid curves) were computed from Eq. 2 with the geometric parameters \( \alpha = 0, 60, 50; \beta = 100, 20, 15; \gamma = 0, 80, 80 \) in (A) and (B), (C) and (D), and (E) and (F), respectively. The feedback parameters \( a \) and \( b \), and the directional gain \( c \), were 0.4, 15.0, and 0.125 in the experiments, and 8.0 × 10⁻³, 0.06, and 2.5 × 10⁻⁵ in the simulations. The scale bar in (E) is 2.0 mm.
Simulations were carried out with \( c = 1.0 \) and 3.0 in the barrier region. The gain \( c \) is set to a constant value, \( c = 1.0 \), and reflecting from barriers. As the wave crosses the barrier (indicated by the rectangle), the gradient is set to a constant value, \( \text{grad}(G) = 0.75 \), until it leaves the barrier region, where the gradient is again set to zero. The gradient term is determined by the mutual interaction according to Eqs. 1 and 3. The time interval between snapshots is 0.2 dimensionless time units. The interaction strength is the same for each wave (\( c = 0.01 \) in Eq. 1), they settle into a stable orbit, where their separation in the orbit is maximized. Figure 4D shows the wave trajectories for several orbits after the initial interaction between the waves (shown by the overlay of successive snapshots). Also shown are the waves relaxing back to the orbit after being perturbed away from the orbit, demonstrating that the orbit formed by the wave pair is stable.

Our experiments and simulations demonstrate how different modes of feedback can be combined to give patterns of spatiotemporal behavior that otherwise would not be possible. The primary feedback stabilizes waves that would not exist in the autonomous system. The wave-guiding excitability gradient, determined by the secondary feedback, permits a wide variety of wave patterns. This gradient represents a truly spatiotemporal feedback, as opposed to spatially homogeneous variations applied in global feedback. There is great flexibility in the design of spatiotemporal feedback, with the linear form used here being easily implemented but only the simplest possibility. Even the linear form, however, represents a dynamic combina-
tion of positive and negative spatiotemporal feedback that is able to accurately direct wave propagation.

The control methods presented here also represent potential tools for investigating spatiotemporal dynamical systems. Our study has demonstrated that there is a direct proportionality between wave trajectory curvature and the excitability gradient for a given wave size (24). Control methods also provide a means for probing underlying mechanisms, as demonstrated in studies of homogeneous chemical systems (25, 26). Such techniques are closely related to the relaxation methods developed by Eigen and co-workers (27) for probing chemical kinetics. Spatiotemporal behavior is pervasive in living systems, and control methods offer a promising direction for probing their underlying mechanisms.

References and Notes
12. A fresh silica gel medium was prepared before each experiment by acidifying an aqueous solution of 10% (v/w) Na2SiO3 and 1.0 × 10−4 M Ru(bpy)32+ with H2SO4. The gel was bathed in a catalyst-free BZ solution of 0.28 M NaBrO3, 0.05 M malonic acid, 0.0002, uth 0.01, Dc = 0.1, the time step df = 0.001, and the spatial grid dx = 0.02. Control of wave motion was carried out using Eq. 1 analogous to the experimental study, except that the wave area was determined by counting pixels with the variable u above a threshold value u th.
17. The control algorithm guides the wave along the target trajectory, generated by advancing the free parameter in Eq. 2. In the case where the trajectory intersects itself, we require the control algorithm to follow the advancing target trajectory.
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A Reversible Solid-State Crystalline Transformation in a Metal Phosphide Induced by Redox Chemistry

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We demonstrate low-potential intercalation of lithium in a solid-state metal phosphide. A topotactic first-order transition between different but related crystal structures at room temperature takes place by an electrochemical redox process: MnP4 ↔ Li,MnP4. The P–P bonds in the MnP4 structure are cleaved at the time of Li insertion (reduction) to produce crystalline Li,MnP4 and are reformed after reoxidation to MnP4 thereby acting as an electron storage reservoir. This is an unusual example of facile covalent bond breaking within the crystalline solid state that can be reversed by the input of electrochemical energy.

Crystalline transformations in the solid state are kinetically hindered reactions that typically occur on geological time scales without the benefit of high temperature, owing to the difficulty of transport within the bulk. An exception is intercalation, where ions are inserted and extracted within gaps in low-dimensional lattices with no substantial change to the lattice itself (7). These processes can take place at ambient conditions because of the minimal restructuring involved. They form the basis on which lithium-ion batteries function—namely, simultaneous reversible (de)intercalation of lithium ions at both high-potential (positive) and low-potential (negative) electrodes (2). Although all positive materials operate on this principle, graphitic carbon, used commercially, is the only material to display classical intercalation behavior at low potential (<1.0 V). Li3Ti2O7 can intercalate one Li, but does so at a higher potential of 1.55 V (3). Other promising materials recently suggested for negative electrodes reversibly uptake lithium by other processes. These include alloying reactions in Li2Sn or Li2Sb nanophases (4, 5), “uptake” by amorphous metal nitrides (6, 7), and reduction to nanophasic metal or suboxide particles in metal oxides (8, 9). Reaction of Li in the intermetallic phase Cu6Sn5 was reported to involve low-potential Li insertion involving Sn displacements within the lattice (10), although the breadth of the x-ray reflections made identification of the Li-rich phase ambiguous. Later evidence suggests that, during deep Li insertion, Sn is extruded from the lattice and Li-Sn alloying is responsible for Li uptake (11).

Here, we demonstrate low-potential intercalation behavior in a solid-state compound based on a metal phosphate. Phosphides lie between the more ionic nitrides and the intermetallic antimonides in their chemistry, but to date, little is known of their electrochemical behavior. We show that a topotactic first-order transition be