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Chemical waves with line defects in the Belousov-Zhabotinsky reaction

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We report our experimental observations of line-defected chemical waves in a quasi-two-dimensional reaction-diffusion system of Belousov-Zhabotinsky reaction. The observed line defects are explicit, which can be directly monitored in real time. In the parameter space, the state of the chemical waves with line defects is located between two regimes of the defect-mediated turbulence. The line defects appear in target waves as well as in spiral waves. We demonstrate that the line defects come out in traveling waves as the later reorganize their spacial topologies to adapt to the change in the local dynamics from simple to complex oscillations or vice versa.

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I. INTRODUCTION

Deterministic temporal chaos in chemical reaction systems, especially in the Belousov-Zhabotinsky (BZ) reaction, has been well studied in the last 20 years [1–5]; its characteristic behavior has been well understood by the concept of stranger attractor and the methods such as phase portraits of the reconstructed attractors, Poincaré sections, return maps, and generalized Renyi dimensions [6–9]. A natural extension on this line of research is to understand the spatiotemporal chaos in spatially extended chemical systems, where the embedding dimension of the dynamics is very high and one may expect to observe high-dimensional chaos. An interesting phenomenon was discovered by Goryachev and Kapral [10–12] in their numerical simulations. They asked the simple questions: What happens when chemical chaotic oscillators, which are generated from a period-doubling cascade, are coupled by diffusion to form a reaction-diffusion system, and what happens when a spiral defect is introduced in the system? They found that the introduction of a spiral defect can stabilize a local region near the spiral core where the system becomes periodic instead of chaotic, and ordered spiral waves self-organized near the spiral core that suppress spatiotemporal chemical turbulence. The most striking feature of the complex periodic spiral waves is the existence of the "line defect," which is a synchronization curve where two loops of periodic cycle exchange and the local dynamics on what is effectively period-1 (P1). Line defects were demonstrated to arise from the reconciliation of the conflict between the global topological organization of a spiral and the topological phase space structure of the local dynamics [10]. The phenomenon is believed to be generic in complex-periodic spiral waves and has been recently observed experimentally by Park and Lee [13].

In the experiments of Park and Lee [13,14], the line defects are themselves spiral curves, which cannot be recognized directly in raw charge-coupled device (CCD) images. They are hidden behind and can only be seen after the images were processes by a transformation. In this paper we investigate experimentally the behavior of traveling waves when the local dynamics becomes complex oscillatory in the medium of the Belousov-Zhabotinsky (BZ) reaction. Another type of line defect is discovered. The defects we find are explicit and can be seen directly in the raw images recorded from the reaction-diffusion system. Usually they are stationary and not spiraling lines, which are in contrast with the previous findings. The line-defected chemical waves are discontinuous, and except along the line defect, the waves are both spatially and temporally period-2 (P2). In the parameter space, the state of the chemical waves with line defects is located between two regimes of the defect-mediated turbulence. We also show that the line defects are quite general in the regime of BZ reaction we explored, and can even occur in concentric or target waves. Our findings are supported by numerical simulations with the Rössler model.

In the next section, we introduce our quasi-two-dimensional spatial open reactor. The main experimental result is given in Sec. III where we present a systematic study of the line defect generation and characterize the state of line-defected chemical waves. We emphasize that line-defected target waves are possible in the system. Section IV presents the result of our numerical simulation using the Rössler equation. We show that our experimental observation can be simulated using a three-variable reaction-diffusion model. We conclude this paper in Sec. V.

II. EXPERIMENTAL SETUP

The experiments are conducted in a spatial open reactor using the ferroin $(\mathrm{Fe(phen)}_3^{2+})$ catalyzed BZ reaction; the experimental setup is the same as described in our earlier studies [15–18]. The heart of our reactor is a thin porous glass disk, 0.4 mm in thickness and 20 mm in diameter. The glass disk has 25% void space and 100 Å average pore size, so that it can be considered as a homogeneous medium for a macroscopic pattern with a character length scale of a few hundred micrometers. The porous glass prevents any convection when used as the reaction medium, so that the reaction-diffusion feature is guaranteed. Each side of the disk is contacted by a reservoir (10 ml in volume) where the reactants are continuously refreshed by highly precise chemical pumps

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(Pharmacia P-500) and kept homogeneous by stirring. The chemicals are feed to both reservoirs separately so that we can keep one (A) in the reduced state of the reaction system, and the other (B) in the oxidized state. When the reactants diffuse into the porous glass and meet there, pattern-forming reactions take place and spatiotemporal patterns form. The chemical patterns are monitored in transmitted light (halogen light filtrated to a wavelength less than 550 nm) with a CCD camera. The signal received by the CCD camera is sent to a computer where images are digitized and saved for further quantitative analysis.

Since there are multiple concentration gradients across the reaction medium, the observed pattern is quasi-three-dimensional, and an instability in the gradient direction may happen [19]. This type of instability was observed in our earlier experiment [20]. In this study we carefully avoid the region in the parameter space where the gradient-induced instability takes place. In the regime of our experiments, the patterned layer is thin [it is estimated to be less than 0.2 mm from continuous stirred tank reactor (CSTR) experimental data], so that the waves in this dimension are well entrained [20,21] and instabilities in this dimension could be avoided. As a result, the observed patterns can be considered as quasi-two-dimensional.

Most previous researches carried out in the BZ reaction were focused on its excitable or simple periodic regimes. Wave patterns in complex periodic regimes were never discussed except for the recent work of [13,14]. The present experiments focus on the regimes of spatiotemporal chaos where the reentry from spiral turbulence into ordered spiral waves occurs [18]. We choose the concentration of malonic acid in reservoir A ($[\mathrm{CH_2(COOH)_2}]^A$or $[MA]^A$) and sulfuric acid in reservoir B ($[\mathrm{H_2SO_4}]^B$) as the control parameters, which are adjustable in a range of $0.2M$ to $0.4M$ and $0.4M$ to $1.2M$, respectively. Other conditions are kept fixed during the whole experiments: $[\mathrm{NaBrO_3}]^{A,B}=0.6M$; $[\mathrm{KBr}]^A=0.03M$; $[\mathrm{ferroin}]^B=1.0$ mM. The flow rate for each side of reservoir is fixed at 36 ml/h, so that the resident time in each reservoir is 10^3 s. The ambient temperature is $25\pm0.5\,°\mathrm{C}$. When we apply a set of control parameters for the reaction, a CCD camera record is taken after a sufficient long time (around an hour) when the pattern relaxes to its asymptotic state.

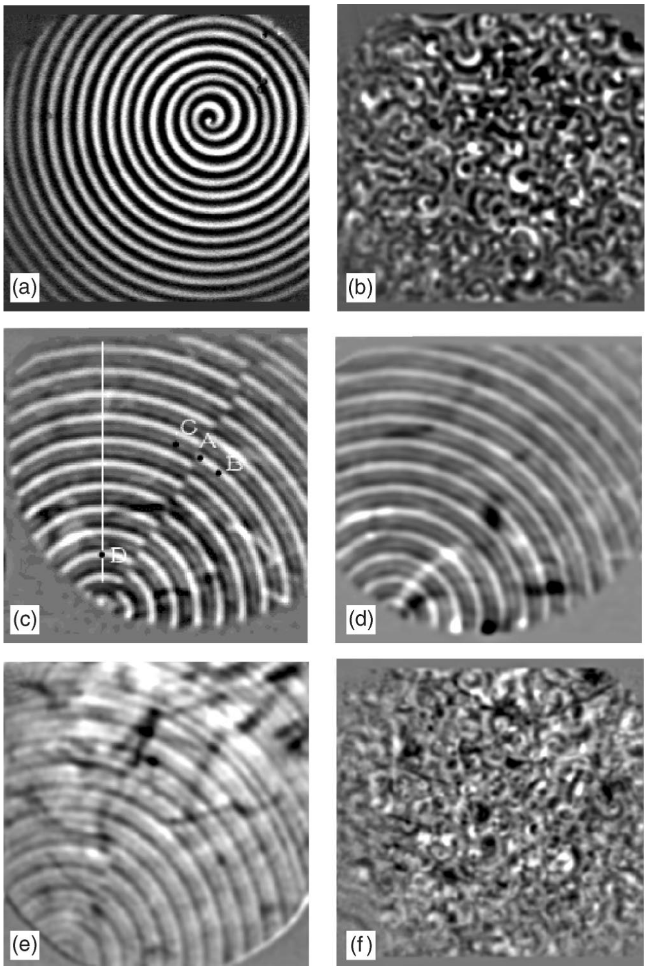

FIG. 1. Snapshot pictures illustrate the pattern dynamics as the concentration of $[\mathrm{H_2SO_4}]^B$ is adjusted. (a) Ordered spiral waves, $[\mathrm{H_2SO_4}]^B=0.400M$; (b) defect-mediated turbulence, $[\mathrm{H_2SO_4}]^B=0.533M$; (c) reentry of ordered spiral waves with line defect, $[\mathrm{H_2SO_4}]^B=0.633M$; (d) ordered spiral waves without line defects, $[\mathrm{H_2SO_4}]^B=0.633M$; (e) line-defected spiral wave near the onset defect-mediated turbulence, $[\mathrm{H_2SO_4}]^B=0.700M$; (f) a state of defect-mediated turbulence, $[\mathrm{H_2SO_4}]^B=0.867M$. The other control parameter is kept fixed at $[\mathrm{MA}]^A=0.3M$.

III. EXPERIMENTAL RESULT

In the first series of experiments, we fix $[MA]^A=0.3M$ and study the dynamical behavior of the system as a function of $[\mathrm{H_2SO_4}]^B$. At $[\mathrm{H_2SO_4}]^B=0.4M$ and with an initial state of single spiral center, we observe a meandering spiral, which is stable and occupies the whole domain of the reactor, as shown in Fig. 1(a). As the concentration of $[\mathrm{H_2SO_4}]^B$ is increased, the dynamics transforms from ordered spiral waves to defect-mediated turbulence due to the Doppler instability [1]. Figure 1(b) demonstrates a snapshot of the turbulence state at $[\mathrm{H_2SO_4}]^B=0.533M$. As $[\mathrm{H_2SO_4}]^B$ is further increased, a new scenario takes place: stable traveling waves grow up from the sea of turbulence. They sweep the defects sea out of the boundary and finally take up the whole domain of the reaction medium. Figure 1(c) depicts such traveling waves at $[\mathrm{H_2SO_4}]^B=0.633M$. The most striking feature in the demonstration is the long *line defect* that crosses the waves, which is explicit and can be directly observed. We record the time series of a point on the line of defect (A) and its two nearby points (B and C) on the opposite sides of the line defect. The evolution data are shown in Fig. 2(a). One observes that the time evolution for the point on the line defect is effectively in the state of P1 oscillations; while those for its two neighbor points are in the state of P2 oscillations with opposite oscillation phases. The chemical waves which are line defected are discontinuous. Except along the line defect, the waves are thereby both spatially and temporally in the P2 state. The spatial profile along the line marked across the image in Fig. 1(c) is obtained and depicted in Fig. 2(b). The two-peak pattern indicates that the reaction medium has a P2 local dynamics. The source of such traveling waves that

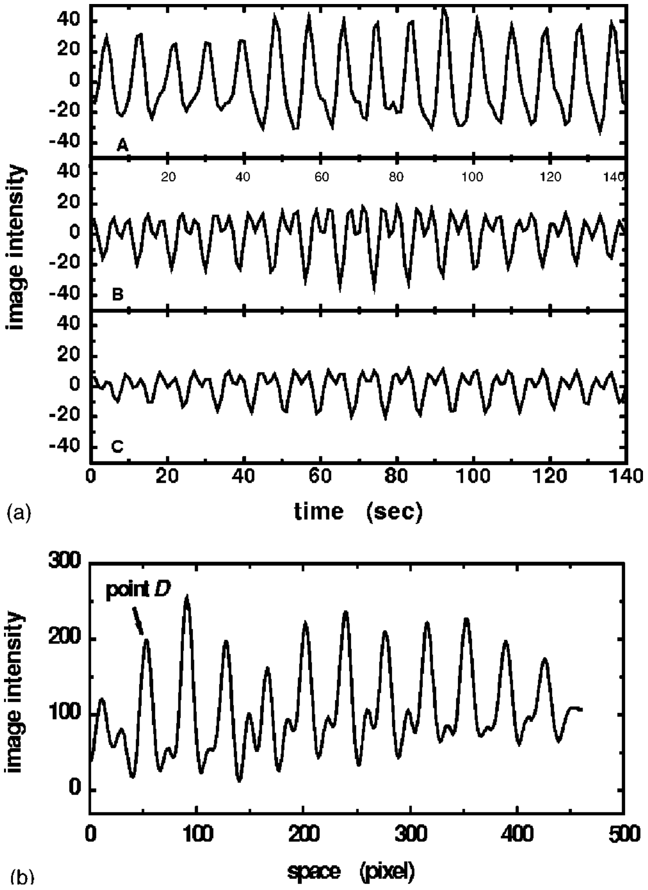

FIG. 2. (a) The time series taken for the points on the line defect and its two opposite neighbors, marked A,B,C in Fig. 1(c), respectively. (b) The spatial profile taken for the cut line in Fig. 1(c) at an instance of time.

carry a line defect located at the boundary of the reaction medium and the waves are suspiciously concentric or target waves. When the $[\mathrm{H_2SO_4}]^B$ reached a high enough value of $0.7M$, defects appear far away from the source of the waves, and the core of stable waves begin to be invaded by the sea of spiral defects little by little again [Fig. 1(e)]. Finally, the spiral turbulence dominates the whole domain [Fig. 1(f)] at $[\mathrm{H_2SO_4}]^B=0.867M$. We repeat this series of experiments a few times; the phenomena are mostly repeated. However, with the same control parameters of Fig. 1(c) where the line defect shows up, we occasionally find that traveling waves (suspiciously targets) without defects, as shown in Fig. 1(d). The line defect in Fig. 1(c) is stationary in our experimental time. We observed no evident movement of the defect during more than an hour.

Similar scenarios take place when we set the other control parameter to $[MA]^A=0.2M$ and $[MA]^A=0.4M$ and repeat the above process. A noticeable phenomenon we observe is that the P2 wave state where line defects can occur is often substable under certain control parameters. It can break down into spiral turbulence in several minutes then regrow up later, or just hold on for a very long time. The turbulence and P2 waves are then in a state of competition. In the process as $[\mathrm{H_2SO_4}]^B$ is decreased from $1.2M$ to $0.7M$ at $[MA]^A=0.4M$, the line defects are unexceptionally observed when stable traveling waves arise. In fact, line defects are quite general in the regime of the BZ reaction we explore, and they can occur in different shapes and appear in various kinds of environments. The defects can be a perfectly straight and long line over P2 traveling waves, which cross the major domain of the viewing area [see Fig. 1(c)]. They can occur some distance away from the wave center or just appear irregularly anywhere in the waves, which confirms the findings of Park and Lee [13,14]. Most defects observed in our experiments are static in our observation time (1 h), but the dynamic line defect is also possible. Figures 3(a) and 3(b) demonstrate such line defects, which look like a belt that rotates steadily [13]. We also checked the effect of the flow rate of the reaction. With other conditions fixed as to what we used before, the flow rate is adjusted to go through 6 ml/h, 12 ml/h, 18 ml/h, 36 ml/h, 48 ml/h, 72 ml/h, and 90 ml/h in both reservoirs, respectively. The phenomena are similar and no remarkable effects on the line-defected waves are found. This experiment rules out the boundary effect on the interface between the reaction medium and reservoirs.

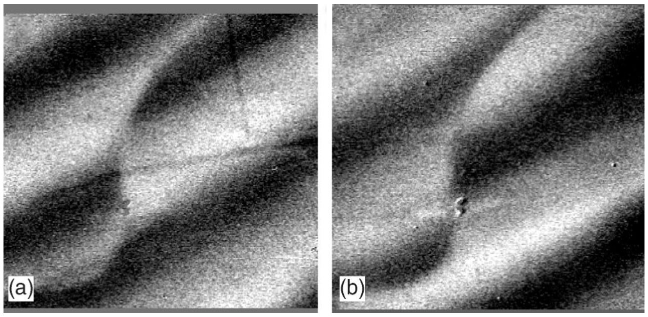

FIG. 3. Examples of rotational line defects generically observed in the experiment.

IV. NUMERICAL SIMULATIONS

Previous theory [10–12] and experiments [13,14] demonstrated that line defects are the prominent feature of complex-periodic spirals. Our experiment indicates that the line defect can actually occur in some more generic circumstances. Actually, the traveling waves where we observe line defects are not apparent spiral waves in all our experimental findings. Instead, they are suspiciously concentric waves. In fact, we found experimentally defects in concentric waves which locate some distance away from the target pacemaker.

In order to demonstrate that line defects are possible in other circumstances than spiral waves in a complex-oscillatory medium, we conduct numerical simulations for the case of target waves as the reaction dynamics is tuned from a state P1 to a state of P2. The model we use is the Rössler equation which is in the following form:

$$\frac{\partial c(r,t)}{\partial t} = R(c(r,t)) + D\nabla^2 c(r,t), \tag{1}$$

where $c(r,t)$ is a vector of local concentrations, D is the diffusion coefficient matrix, and $R(c(r,t))$ describes the local reaction kinetics: $R_x=-c_y-c_z, R_y=c_x+Ac_y, R_z=c_xc_z-Cc_z+B$.

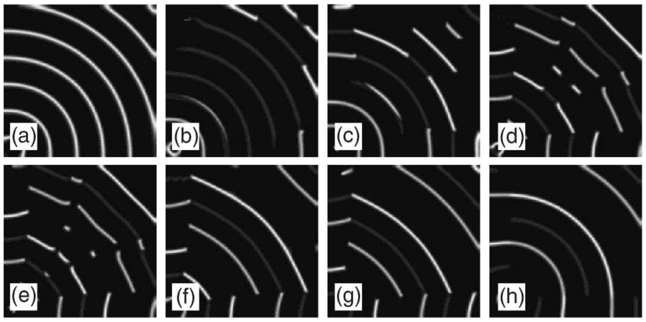

FIG. 4. Numerical simulation of target waves with the Rössler model when the local dynamics undergoes a transition from P1 to P2 oscillation. The pacemaker is located at the bottom-left corner. (a) A snapshot of a target wave and (b), (c), (d), (e), (f), (g), and (h) depict the evolution process after the P1-to-P2 transition is turned on. Parameters: $A=B=0.2$, $D=0.05$, and $C=2.5$ for (a) and 3.5 for (b), (c), (d), (e), (f), (g), and (h).

A,B,C are the control parameters. We numerically simulate its dynamics on a lattice. An inhomogeneity is introduced into the system by fixing the local concentrations for a point in the bottom-left corner of the lattice. From the pacemaker of the inhomogeneity, a target wave grows up [Fig. 4(a)], which is both spatially and temporally in the state of P1. As the target wave is fully grown, the local dynamics is tuned from P1 to P2. The P1 target is eventually transformed into a P2 concentric wave through a very long transient journey. In the transition process, the line defects in the traveling waves are observed [see Figs. 4(f) and 4(g)]. The line defects, which truncate the waves, evolve very slowly; they merge and finally disappear in the lattice as the full reorganization of the spatial and temporal topology is finished to form a P2 target. Similar behavior is observed as the pacemaker is placed in the center of the lattice and we repeat the above evolution.

It is worthy of note that the Rössler model we simulated above is not a chemical model in nature because it does not guarantee non-negative variables for chemical concentrations. We choose this model in our simulation only for the purpose of convenience because theoretical models, which are required to have periodic-doubling cascades for the problem in discussion, that actually describe the BZ reaction are usually complex and are not numerically convenient. Actually, the nonchemical nature of the Rössler model does not affect the generality of the phenomenon of line-defected waves we found numerically above. We checked the Willamowski-Rössler model, which is a chemical version of the Rössler equations that has a chemical nature, in its regimes of periodic-doubling cascade and find very similar results as reported in Fig. 4. While the phenomena of line-defected spiral waves in complex oscillatory media have been clarified both theoretically and experimentally, our above numerical findings indicate that the line defect can also possibly occur as a long-lived transient behavior in the case of target patterns, and that the chemical waves we observed in the BZ reaction can be line-defected targets.

A disagreement exists between experimental result and numerical simulation on the asymptotical state of line defects in target waves. In the experiment we observe stationary line defects while in the numerical simulation all the line defects are transient. A theoretical analysis needed to be carried out to finally resolve this disagreement.

V. CONCLUSION

In summary, we report line-defected complex-periodic traveling waves in the BZ reaction. The line defects appear quite generally in the regime of the BZ reaction we explored and are explicitly observable in raw CCD images. They usually are stationary or move very slowly in the system. The discontinuous waves are complex-periodic both in space and time except on the line defects. In contrast with previous experimental findings where line defects were usually spiraling lines and hidden behind in spiral waves, the line defects we found are explicitly displayed, and particularly, they do not necessarily occur in complex-periodic spiral waves. Line defects have been known as a prominent feature of complex-periodic spiral waves and were regarded as the result of reconciliation of the spatial topology of the spiral and its local multiperiodic local dynamics. Our experimental results indicated that line defects can occur in more generic circumstances of chemical waves such as concentric wave patterns. The line defects occur generally in traveling waves in complex oscillatory media. As the local dynamics of the medium undergoes a bifurcation (e.g., periodic doubling) and changes from simple into complex periodic oscillation or vice versa, line defects can show up in traveling waves as they reorganize their spacial topologies to adapt for the change in local dynamics, as our numerical simulations with the Rössler model demonstrated. When the control parameter in our experiment is adjusted in the regime of turbulence, the local dynamics can undergo a backward periodic-doubling bifurcation from chaos to ordered periodic oscillations. When this happens and ordered wave patterns that appear thereby adjust their spatial structures, line defects come out as a result.

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[1] R. A. Schmitz, K. R. Graziani, and J. L. Husdon, J. Chem. Phys. **67**, 3040 (1977).

[2] J. C. Roux, R. H. Simoyi, and H. L. Swinney, Physica D **8**, 257 (1983).

[3] J. Turner, J. C. Roux, W. D. McCormick, and H. L. Swinney, Phys. Lett. **85A**, 9 (1981).

[4] K. C. Coffman, W. D. McCormick, Z. Noszticzius, R. H. Simoyi, and H. L. Swinney, J. Chem. Phys. **86**, 119 (1987).

[5] F. W. Schneider and A. F. Münster, J. Phys. Chem. **95**, 2130 (1991).

[6] D. S. Broomhead and G. P. King, Physica D **20**, 217 (1983).

[7] R. Badii and A. Politi, Phys. Rev. Lett. **52**, 1661 (1984).

[8] F. Argoul, A. Arnéodo, and R. Richetti, Phys. Lett. A **120**, 269 (1987).

[9] W. Van de Water and P. Schram, Phys. Rev. A **37**, 3118 (1988).

[10] A. Goryachev and R. Kapral, Phys. Rev. E **54**, 5469 (1996).

[11] A. Goryachev, H. Chaté, and R. Kapral, Phys. Rev. Lett. **80**, 873 (1998).

[12] A. Goryachev, H. Chaté, and R. Kapral, Phys. Rev. Lett. **83**, 1878 (1999).

[13] J. S. Park and K. J. Lee, Phys. Rev. Lett. **88**, 224501 (2002).

[14] J. S. Park and K. J. Lee, Phys. Rev. Lett. **83**, 5393 (1999).

[15] Q. Ouyang, H. L. Swinney, and G. Li, Phys. Rev. Lett. **84**, 1047 (2000).

[16] L. Q. Zhou and Q. Ouyang, Phys. Rev. Lett. **85**, 1650 (2000).

[17] L. Q. Zhou and Q. Ouyang, J. Phys. Chem. A **105**, 112 (2001).

[18] H. Y. Guo, L. Li, Q. Ouyang, J. Liu, and Z. S. She, J. Chem. Phys. **118**, 5038 (2003).

[19] P. Blanchedeau, J. Boissonade, and P. De Kepper, Physica D **147**, 283 (2000).

[20] C. Zhang, H. Zhang, Q. Ouyang, B. Hu, and G. H. Gunaratne, Phys. Rev. E **68**, 036202 (2003).

[21] D. Winston, M. Arora, J. Maselko, V. Gáspár, and K. Showalter, Nature (London) **351**, 132 (1991).