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Oscillatory and Chaotic States of the Electrical Conduction in Barium Sodium Niobate Crystals

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Evidence is presented for oscillatory and chaotic behavior of the electrical conduction measured in barium sodium niobate single crystals at elevated temperatures. Analysis of the chaotic state verifies the existence of a strange attractor, whose dimension and entropy are determined. The observations indicate a Ruelle-Takens-Newhouse scenario.

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Nonlinear physical systems which exhibit chaotic behavior have recently aroused much attention.[1] As far as electrical conduction is concerned, self-generated oscillations have been observed in various substances [see, for instance, Keizer and coworkers,[2-5] and for barium sodium niobate (BSN) especially the paper by Voronov and Kuz'minov[6]]. However, only a few systems have been studied for deterministic chaotic behavior.[7-10]

In this Letter we show that the dc-induced electrical conduction of BSN crystals (barium sodium niobate, stoichiometric composition $Ba_2NaNb_5O_{15}$) can behave in a stationary, oscillatory, or chaotic manner, depending on the choice of the control parameters. BSN crystals exhibit a nonlinear I, U characteristic,[11] which we suppose is due to a mixed electronic-ionic conduction mechanism. A detailed model describing the electrical conduction in BSN will be published elsewhere.

Our experiments are performed with BSN single crystals grown in our laboratory.[12] The sample (size $\approx 3\times3\times5$ mm^3) is placed in a heating oven through which a constant flow of humidified oxygen is maintained. After an annealing process at 800 °C, a stabilized dc current is applied to the sample along the c axis employing Pt paste electrodes. We measure the voltage across the crystal. Simultaneously, an image of the crystal is projected perpendicular to the field direction onto a screen, with use of crossed polarizers to observe the birefringence pattern of the crystal.

The control parameters are the crystal temperature, current density, and flow rate of humidified oxygen. Depending on their setting we observe quite different time dependences of the voltage: With fixed current density (1 mA/cm^2) and oxygen flow rate (1 L/h) we measure at temperatures above 600 °C a time-independent voltage. At around 600 °C self-generated voltage oscillations are observed which can be sustained for days. Below a temperature of about 500 °C the oscillatory state becomes unstable and a chaotic state develops via intermediate states. At temperatures lower than about 300 °C the voltage becomes stationary again. Between temperatures of 300 and 600 °C we observe typical time constants of 10 min to 1 sec and amplitudes from over 100 V down to about 1 V.

Figure 1 shows a transition from the oscillatory [Fig. 1(a)] to the chaotic state [Fig. 1(c)] as the crystal temperature is decreased. The transition includes intermediate states such as shown in Fig. 1(b). Apart from the measured time dependences of the voltage the corresponding phase portraits are also illustrated in Fig. 1: The voltage $U(t_k+\tau)$ is plotted versus $U(t_k)$. We note a single closed loop [Fig. 1(d)], a diffuse ring [Fig. 1(e)], and finally an

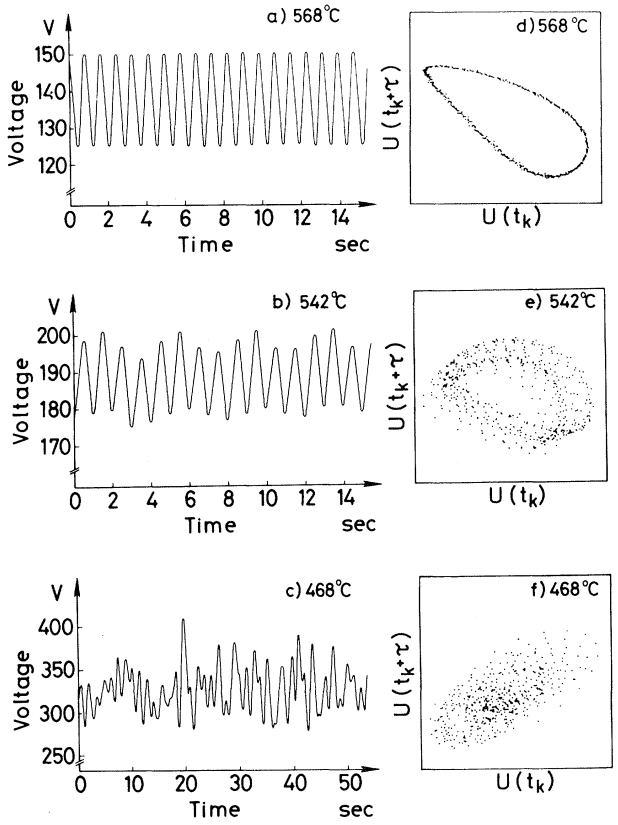

FIG. 1. Self-generated oscillations of the voltage $U(t)$ and corresponding phase portraits $U(t_k+\tau)$ vs $U(t_k)$ ($k=1$–500 is the index for the sampling points; $\tau=0.3$ sec is the time delay). The temperature is varied; the current density (1.8 mA/cm^2) and oxygen flow rate (1 L/h) are held constant. Note the change of scale in (c).

irregular pattern [Fig. 1(f)].

Simultaneous with the oscillations, the birefringence pattern of the crystal is seen to be locally disturbed: A "domain" emerges from the cathode as the voltage increases to the maximum, and disperses gradually during its movement through the crystal as the voltage relaxes to the minimum. Measurements of the voltage across each of three successive sections of the crystal, made with use of intermediate platinum wire loop electrodes, show that a region of high resistivity progresses through the crystal. In the chaotic state each voltage peak appears to be associated with an optically observed domain.

In order to characterize the transition into the chaotic state we compute the Fourier spectra of the voltage signals. In Fig. 2 the normalized spectra are shown for the measurements of Fig. 1. In the oscillatory state we see the fundamental frequency f_1 with its higher harmonics [Fig. 2(a)]. In the intermediate state a second frequency f_2 and linear combinations of f_1 and f_2 are seen [Fig. 2(b)]. The frequency ratio is temperature dependent; we measure $f_1/f_2=3.94$ at 542 °C. A further form of the intermediate state is shown in Fig. 2(c) where a third fundamental frequency f_3 appears in the spectrum together with linear combinations of f_1, f_2, and f_3. The time dependence of the voltage in this state is not given in Fig. 1 as it looks similar to that of Fig. 1(c). In the chaotic state [Fig. 2(d)] the spectrum shows a substantial increase of broadband noise at low frequencies: This broadband is centered

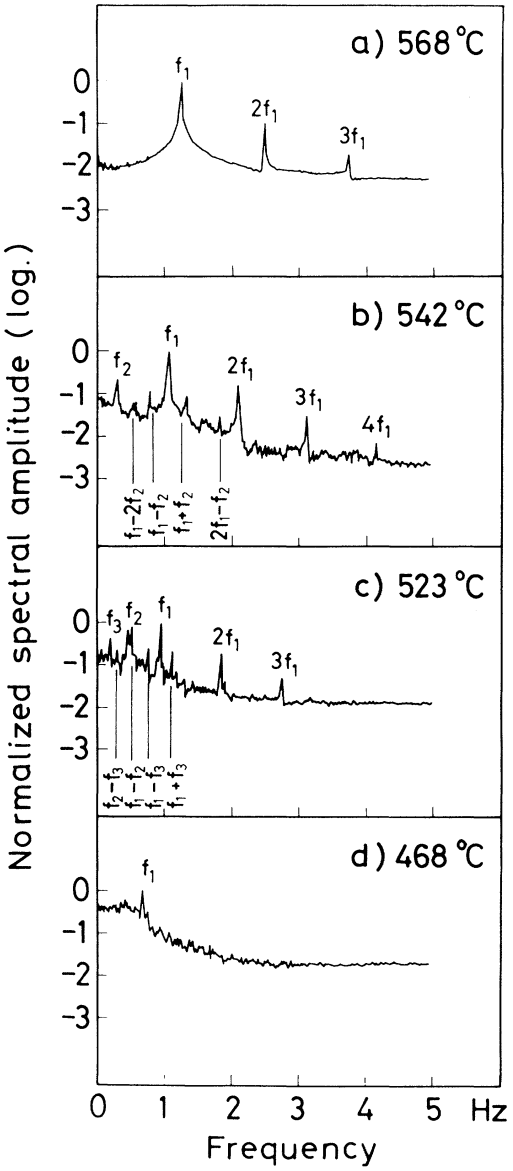

FIG. 2. Normalized spectra of $U(t)$ in the (a) oscillatory, (b),(c) intermediate, and (d) chaotic states. The spectral amplitude is normalized in relation to the maximum of the highest peak. In (b) and (c) two and three fundamental frequencies, respectively, are seen.

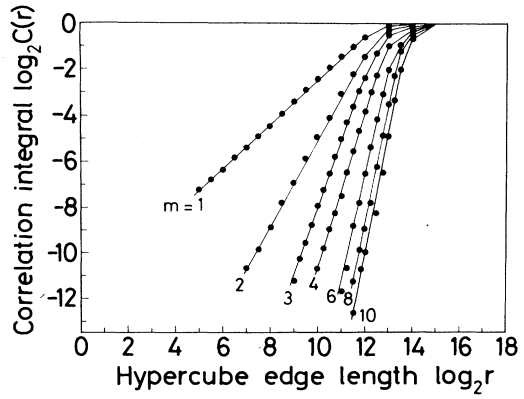

FIG. 3. The correlation function $C(r)$ calculated from the measured voltage signal of Fig. 1(c) is plotted vs the hypercube edge length r on a log-log scale for different values of the embedding dimension m. The curves for $m = 5, 7, 9$ are not shown here for reasons of clarity. Number of sampling points $N = 2000$; total observation time $T = 200$ sec.

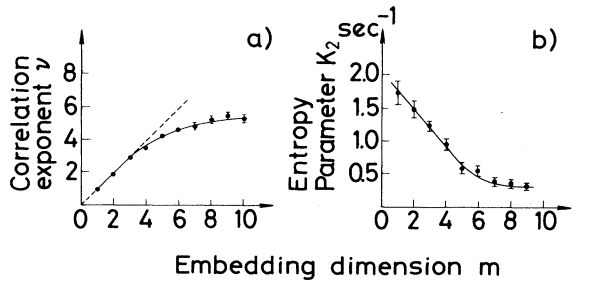

FIG. 4. (a) The correlation exponent ν and (b) the entropy parameter K_2 computed from the data of Fig. 3 are plotted as a function of the embedding dimension m. The curves are drawn only to guide the eye.

around 340 mHz and is about 1.5 orders of magnitude above the noise level. A discrete line at $f_1 = 720$ mHz is superimposed on the band.

The transition from the oscillatory into the chaotic state due to a temperature variation has been observed in most of our experiments with the appearance of only two fundamental frequencies. However, in some of our measurements [as in Fig. 2(c)] we notice three fundamental frequencies prior to the onset of chaos. The appearance of a third frequency has been observed only in few other systems.[13,14] From the observations reported we suppose that our system follows the Ruelle-Takens-Newhouse route[15] into chaos implying the existence of a strange attractor.

In order to study the nature of the chaotic state in a quantitative manner we apply the method introduced by Shaw,[16] Crutchfield and Packard,[17] and Brandstäter *et al.*[18] Following Grassberger and Procaccia[19] we calculate the correlation integral for the measured voltage signal:

$$C(r) = \lim_{N\to\infty} \frac{1}{N^2} \sum_{\substack{i,j=1 \\ i\neq j}}^{N} \Theta(r - \alpha|\vec{X}_i - \vec{X}_j|).$$

N is the number of points and Θ the Heaviside function. α is a scaling factor; here we set $\alpha = 60$ V^{-1}. The vector $\vec{X}_i = \{U(t_i), U(t_i+\tau),\ldots,U(t_i+(m-1)\tau)\}$ is a point in the m-dimensional phase space in which the attractor is embedded. The phase space is divided into hypercubes with a linear dimension r, and all points whose mutual distances are less than r are counted. Grassberger and Procaccia showed that in case of a strange attractor $C(r)$ should scale as r^{ν}, where the correlation exponent ν measures the dimension of the attractor.

In Fig. 3, $\log_2 C(r)$ is plotted as a function of $\log_2 r$ at different values of the embedding dimension m. Hereby we use the data of Fig. 1(c). We note that $C(r)$ indeed scales according to a power law over a wide range of r. With increasing m the curves become steeper and more parallel to each other. The slopes of the curves yield values for ν which are plotted in Fig. 4(a) as a function of m. Note that ν increases at first proportional to m and then approaches an asymptotic value of $\nu = 5.3 \pm 0.2$. This indicates the existence of a strange attractor, whereas in case of a stochastic (noise) signal ν would increase proportional to m for all values of m.

Another dynamical property of a strange attractor is the Kolmogorov entropy which measures the strength of the chaos.[16,17] In an ordered system it is expected to have the numerical value 0, in a random system it should be infinite, and in a chaotic system it is expected to be positive and definite. Grassberger *et al.*[20] showed that the algorithm described above can also be used to estimate the Kolmogorov entropy directly from the measured signal. They pointed out that the correlation integral scales with the embedding dimension m like $C(r) \sim \exp(-m\tau K_2)$ where the entropy parameter K_2 is a lower bound to the Kolmogorov entropy. In Fig. 4(b) the values of K_2 calculated from the data of Fig. 3 are plotted as a function of m. Note that K_2 decreases with m to a value of about $K_2 = 0.4$ $\sec^{-1}$.

The Fourier spectra, the fractal asymptotic value of ν, and the nonzero positive asymptotic value of K_2 present consistent evidence for a strange attractor. We therefore think that BSN provides an attractive new system for the experimental study of

deterministic chaos in nonlinear dynamics.

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