EXCITATIONS IN OPAL PHOTONIC CRYSTALS INFILTRATED WITH POLARIZABLE MEDIA

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Abstracat

Photonic crystals (PC) are a class of artificial structures with a periodic dielectric function. PCs can be a laboratory for testing fundamental processes involving interactions of radiation with matter in novel conditions. We have studied the optical properties of opal PCs that are infiltrated with highly polarizable media such as J-aggregates of cyanine dyes. Opals are self-assembled structures of silica (SiO_2) spheres. We report our studies on clarifying the relationship between a polaritonic gap and a photonic stop band (Bragg gap) when they resonantly coexist in the same structure. Infiltration of opal with polarizable molecules combines the polaritonic and Bragg diffractive effects. Both effects exist independently when the Bragg (at $\omega = \omega_B$) and polaritonic (at $\omega = \omega_T$) resonances are well separated in frequency. A completely different situation occurs when $\omega_T \approx \omega_B$. Such a condition was achieved in opals that were infiltrated with J-aggregates of cyanine dyes that have large Rabi frequency. Our measurements show some dramatic changes in the shape of the reflectivity plateaus, which are due to the interplay between the photonic band gap and the polaritonic gap. The experimental results on reflectivity and its dependence on the light propagation angle and concentration of the cyanine dyes are in agreement with the theoretical calculations.

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Introduction

Photonic crystals (PC) [1, 2] and in particular PC with a complete photonic band gap (PBG) [3] have recently attracted much attention due to their rich physics and possible applications in integrated optics, photonics devices for telecammunication such as tunable lasers, high reflectivity devices [4, 5]. In these systems the dielectric function is periodically modulated and consequently light diffraction effects dominate their optical properties [6].

Among the main possible applications of PCs is the fabrication of low threshold lasers [7, 8, 9], since the photonic density of states can be enhanced for frequencies close to the PBG [1, 2]. Photonic crystals that contain few planned defects are most suitable for laser action. The defects cause localized intra-gap photonic states for which the PC sample acts as a resonator with a very high quality factor, Q [7, 8]. However, photon propagation traffic in and out from the defect-resonator has not been well developed for three-dimensional (3D) PCs [9]. In fact there has been some experimental progress on light propagation inside the PBG and mostly for line defects in 2D PCs [7, 10, 11, 12, 13].

One of major goals of the photonic band-structure calculations is to engineer structures with a complete band gap that have no propagating solutions of Maxwell's equations within the forbidden gap. The frequency gap in the photonic spectrum sets the stage for a number of physical effects. Examples of such effects are inhibition of the spontaneous emission for an emitter with transition frequencies within the gap and enhancement of spontaneous emission at the band edges due to redistribution of the density of states. Other physical effects of the PBG are discussed in the literature [1, 14, 15, 16, 17, 18]. Influence of the PBG on the photo-induced absorption properties was investigated for the first time by the author [19].

The band structure of a material with periodically modulated dielectric constant strongly depends on the periodicity, the symmetry properties, the dielectric constant contrast, the internal structure of the unit cell, and the filling factor of the structure. Also important are the optical properties of the constituents of the photonic crystal (PC), which are related to the atomic and molecular structure of the material. An important example of these properties is polarizability, which determines the shape of the dielectric function.

Homogeneous but frequency-dispersive media comprise another class of materials with a forbidden gap for light propagation. The energy gap in these materials has a polaritonic

origin, i.e., the gap is formed by the interaction of light with the medium polarization. This energy gap can be viewed as a result of anti-crossing between the photonic and phononic/excitonic/plasmonic dispersion branches.

The goal of this article is to clarify the relationship between these two gaps when they exist in the same structure. A theoretical study of the subject has been published by authors [20]

Close packed structures of mono-disperse silica (SiO_2) spheres dubbed opal offer an incomplete PBG, i.e., light propagation is forbidden only along certain directions inside the crystal. The voids between the silica spheres in the opal can be infiltrated with various media, which brings about nontrivial physics. In particular the medium may contain polarizable molecules. As a result of the polarizability there will be an additional gap for propagation of the electromagnetic waves regardless of the periodicity of the PC. Infiltration of the opal with polarizable molecules combines therefore the polaritonic and Bragg diffractive properties. Both effects exist independently when the Bragg ($\omega = \omega_B$) and polaritonic ($\omega = \omega_T$) resonances are well separated in frequency. A completely different situation occurs when $\omega_B \approx \omega_T$. Such a condition was achieved in opals that were infiltrated with highly polarizable medium, and a peculiar *interplay* between the various frequency dispersions was observed. Our measurements have shown some dramatic changes in the shape of the gap, as a result of the interplay between the photonic band gap (PBG) and the polaritonic gap. The experimental results on reflectivity and its dependence on the illumination angle and concentration of the polarizable medium were all in excellent agreement with the theoretical calculations [20, 18].

This research has strongly benefited from discussions with Prof. J. Worlock of the Department of Physics, University of Utah. On our search for the material with desired J-peaks, we got very useful hints from Dr. D. G. Lidzey of The Department of Physics and Astronomy, University of Sheffield.

Theory

The treatment of light propagation along the preferred [111] (or z) direction may be simplified by considering a one-dimensional periodicity of the dielectric function, $\epsilon(z) = \epsilon_0 + \delta\epsilon \cos Kz$ where $\delta\epsilon(\ll \epsilon_0)$ is the modulation amplitude, ϵ_0 is the average dielectric function, $K = \frac{2\pi}{d}$ is the modulation wave-vector, and $d = D\sqrt{\frac{2}{3}}$ is the (111) inter-plane distance. It is easy to show [4] that a gap, with $\Delta\omega_B = \frac{\omega_B \delta\epsilon}{2\epsilon_0}$ centered at $\omega_B = \frac{cK}{2\sqrt{\epsilon_0}}$ is

formed in the photon dispersion relation (Figure 0.1). The two photonic branches at the light wave vector K away from the Brillouin zone edge $\frac{K}{2}$ acquire the form:

$$\omega^{(1,2)} = \omega_B \pm \sqrt{(\frac{2\omega_B}{K})^2 q^2 + \Delta\omega_B^2}, \tag{0.1}$$

where $q = k - \frac{K}{2} \ll k$. These branches are plotted in Figure 0.1(a). In Figure 0.1(b) we plot the calculated Bragg stop band (B) in the reflectivity spectrum. It is worth noting that when light propagates at an angle θ with respect to z, then the Bragg stop band blue shifts according to the relation:

$$\omega_B(\theta) = \omega_B(0)\sqrt{\frac{\epsilon_0}{(\epsilon_0 - \epsilon_1 \sin\theta^2)}}, \tag{0.2}$$

where ϵ_1 is the dielectric constant of the surrounding medium. Our opal PC had a Bragg stop band in air at about 660 nm at $\theta = 0$ and at about 560 nm at $\theta = 45^0$ [21].

The photon dispersion relations and the reflectivity spectrum drastically change [20] when a polarizable medium having a dielectric function $\epsilon(\omega) = \epsilon_\infty[1 - \frac{\omega_{LT}}{\omega - \omega_T}]$ is infiltrated into the opal. Here, ω_T , is the transverse frequency, ω_{LT} is the longitudinal-transverse frequency splitting (with a Rabi frequency splitting $\Omega_P = \sqrt{\frac{\omega_T \omega_{LT}}{2}}$), and ϵ_∞ is the high frequency dielectric constant. In this case, if the dimensionless frequency detuning, $\delta = \frac{\omega_T - \omega_B}{2\Delta\omega_B}$, is not too large (i.e. , $\delta < 1$), then the light dispersion relations near ω_B contain four branches given in a concise form by [20]:

$$Q = \sqrt{(\Delta - \frac{\alpha^2}{\Delta - \delta})^2 - \frac{1}{4}}, \tag{0.3}$$

where $Q = \frac{\omega_B}{K\Delta\omega_B} q$ is the dimensionless wave-vector, $\alpha = \frac{\Omega_P}{2\Delta\omega_B}$ is the Bragg-polariton coupling constant, and $\Delta = \frac{\omega - \omega_B}{2\Delta\omega_B}$ is the dimensionless frequency. These dispersion relations are plotted in Figure 0.1(c) for a detuning $\delta = 0$; the calculated reflectivity spectrum is shown in Figure 0.1(d). It is evident from Figure 0.1(c) as well as from the formulation of the transparent spectral range between the two reflectivity plateaus B_1 and B_2 in Figure 0.1(d), that the braggoriton excitations emerge inside the original unperturbed photonic gap.

For a detuning $\delta \neq 0$ the branches lose their symmetry [20] (Figure 0.1(e)); this can be also seen in the reflectivity spectrum (Figure 0.1(f)). By changing the light

impinging angle θ with respect to the [111] direction, the detuning δ between the Bragg and polariton gaps may be easily changed in opals since $\omega_B(\theta)$ changes with θ (see above), whereas ω_T remains unaffected. We use this mechanism for measuring the dispersion of

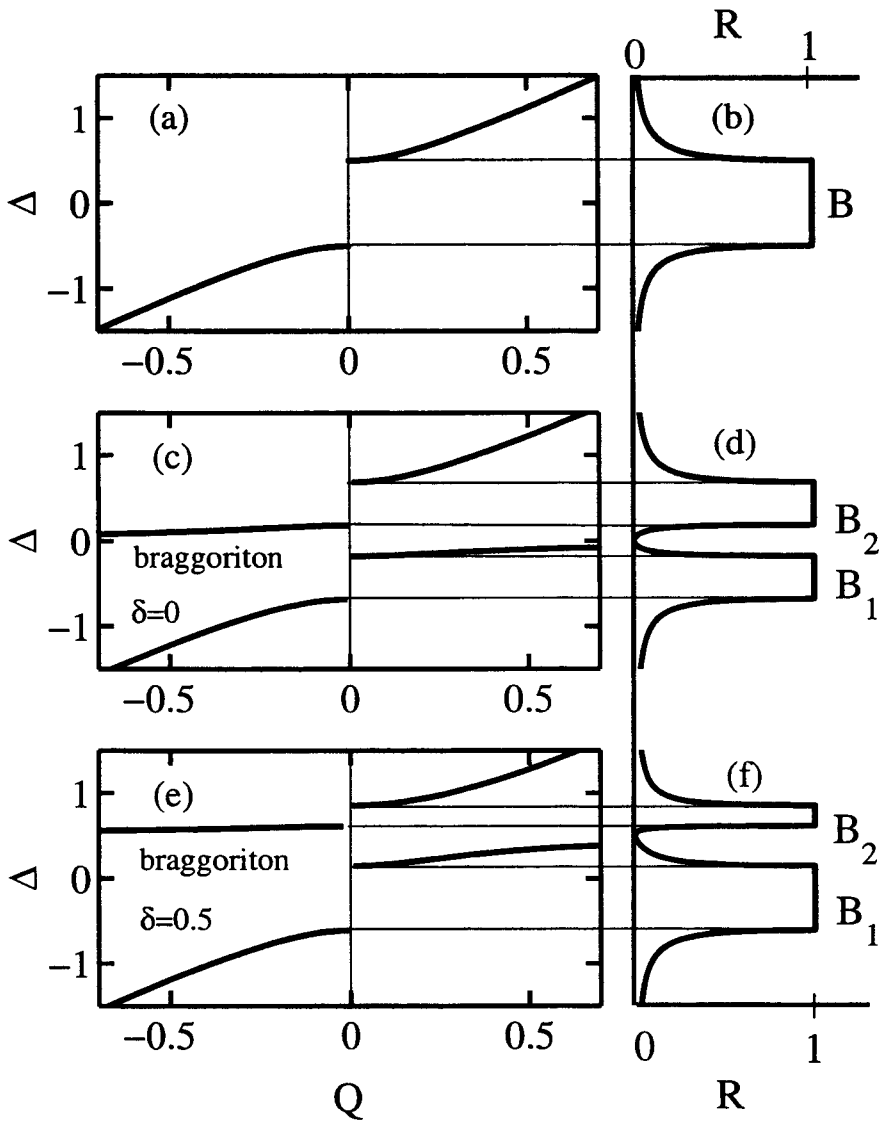

Figure 0.1. The dispersion relations [Δ(Q), where Δ and Q are normalized frequency and wave-vector, respectively (see text)] and reflectivity spectra [R(Δ)] of an uninfiltrated (a) and (b), and uninfiltrated (c)-(f) PC with a highly polarizable dye, for wave-vector Q close to the Brillouin edge (Q = 0). For the infiltrated opal the normalized detuning between the Bragg and exciton/polariton gaps is $\delta = 0$ for (c) and (d) and $\delta = 0.5$ for (e) and (f), whereas the normalized coupling parameter is $\alpha = 0.5$ in both cases. B is the Bragg stop band in reflectivity, whereas B_1 and B_2 are the split stop bands due to Bragg-like and polariton-like gap, respectively.

the braggoriton excitations with θ.

Experiments and discussion

The synthetic opal single crystals used here were cut from a polycrystalline sample obtained by slow sedimentation of a colloidal suspension of silica (SiO_2) spheres (with a mean diameter $D \approx 300$ nm and dispersion in D of about 4%). Since the as-grown opals are weakly bound, sintering at 750^0C was used to achieve robust mechanical properties. This sintering process provides inter-sphere necks joining neighboring silica spheres in a face-centered-cubic (fcc) structure of the opal. Weak iridescence in air results from Bragg diffraction off (hkl) crystal planes, which produce gaps in the reflectivity spectrum at ω_{hkl} [22]. However due to the relatively small contrast between the refraction indices of silica and air, then opal PC does not possess a complete PBG. In general the most pronounced stop band in synthetic opals occurs along the fast growing [111] direction [22], and therefore we conduct our angle-dependence reflectivity measurements off the (111) planes.

For these measurements we infiltrated a large single crystal opal with the cyanine dye NK-2567, or 2,2'-dimethyl-8-phenyl-5, 6, 5', 6'-dibenzothiacarbocynine chloride, of which chemical diagram is shown in Figure 0.2(a), inset. In chloroform solution these cyanine molecules weakly absorb in the yellow part of the spectrum (at $\approx$ 600 nm) and have a moderately strong photoluminescence band in the red [23]. However when a thick chloroform solution of NK-2567 is casted into films on glass substrates, then J-aggregates are readily formed from the cyanine molecules. The cyanine J-aggregates are characterized by a red shifted absorption (or reflectivity) band that peaks at $\omega_T \approx 700$ nm and by greatly diminished photoluminescence band. Under these conditions the reflectivity spectrum can be measured with little or no interference from the emission band. The cyanine molecules were infiltrated inside the opal, and J-aggregate formation was achieved by repeated pulling of the sample through a thick dye solution in chloroform [21]. Uninfiltrated molecules were washed out from the sample surface to eliminate their reflectivity peak in the spectrum, which interferes with the braggoriton bands [24].

The crystal was embarked on a $\theta - 2\theta$ homemade goniometer, where an incandescent, well-collimated light beam was directed at an angle θ with respect to the [111] direction of the opal. The reflected beam at 2θ was dispersed by a monochromator (0.25 m) and its intensity measured by a Si photodiode and a lockin amplifier [21]. At $\theta = 0$

the uninfiltrated opal showed a [111] Bragg stop band in the reflectivity spectrum at $\omega_B(0) \approx 660$ nm; this band red-shifted to $\omega_B(0) \approx \omega_T \approx 700$ after infiltration due to the increase in ϵ_0. Figure 0.2(a) shows the angle-dependent reflectivity spectra of the cyanine-infiltrated opal for θ ranging from 2.5^0 to 30^0. At large θ when $\omega_B(\theta) > \omega_T$, the detuning δ is large and the Bragg stop band (B_1) dominates the reflectivity spectrum. However as θ decreases, $\omega_B(\theta)$ red shifts towards ω_T so that the detuning δ decreases and consequently the Bragg/polariton interaction becomes important. Thus, at decreasing θ another band (B_2) is formed with increasing relative intensity (Figure 0.2(b), inset). At the same time the dispersion of peak B_1 slows down, whereas the dispersion of peak B_2 increases (Figure 0.2(b)). The reason that only a moderate dip between the split reflectivity bands is observed is the unavoidable disorder in the opal sample, which tends to smear out sharp spectral features.

Using Equation (0.3), we fit the frequencies of the Bragg-like B_1 and polariton-like B_2

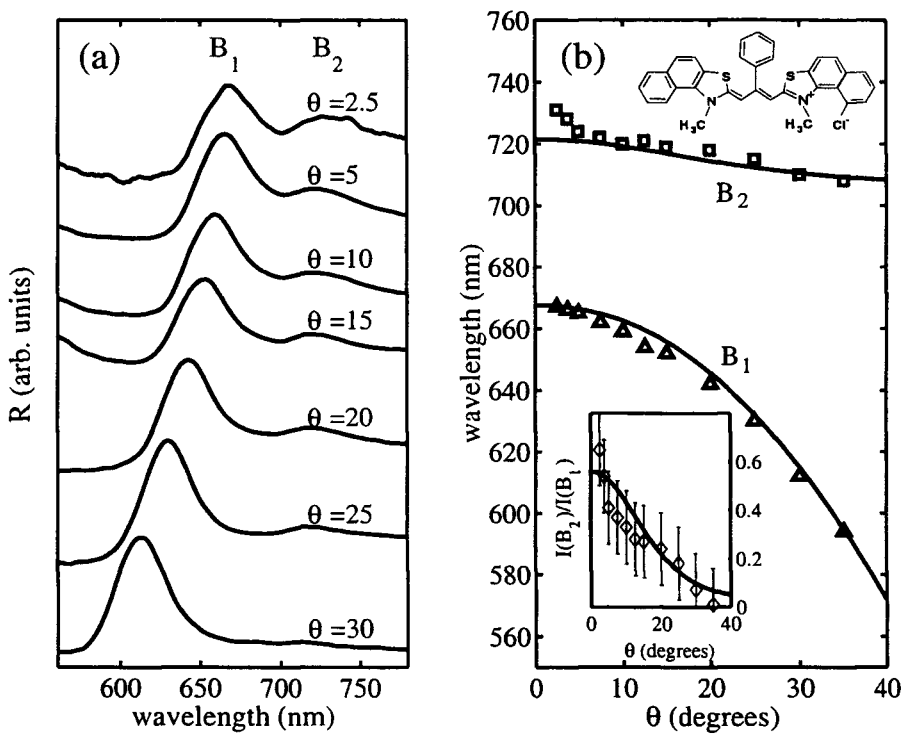

Figure 0.2. The angular dependent reflectivity spectra of an opal PC infiltrated with J-aggregates of NK-2567 cyanine (chemical formula is shown in the inset to (b)) showing the evolution of the two reflectivity bands B_1 (Bragg-like) and B_2 (polariton-like) with the light impinging angle, θ. The frequency dispersion and relative strengths of B_1 and B_2 bands with θ are summarized in (b) and (b) inset, respectively.

reflectivity peaks and their relative intensity vs. θ. Far from resonance the the Bragg polariton interaction is weak and the reflectivity peaks are governed by ϵ_0 and δ. The apparent split between the reflectivity peaks at resonance condition critically depends on α, and their relative intensity is very sensitive to δ (see Figure 0.1(d) and (f)). The calculated frequencies and relative intensities versus θ are shown in Figure 0.2 inset, respectively and compared with the data. The excellent agreement between theory and experiment seen in Figure 0.2 inset was achieved using Equation (0.2) and Equation (0.3) with the following parameters: $\lambda_B = 684$ nm and $\Delta\omega_B = 53$meV (or $\Delta\lambda_B = 20$ nm), which are slightly shifted compared to the values of the uninfiltrated opal; $\lambda_T = 703$ nm ($\delta = -0.46$ at $\theta = 0$), and $\epsilon = 1.4$. The relatively strong Bragg-polariton coupling $\alpha = 0.57$ that we obtained results in a Rabi splitting $\Omega_B = 60$ meV for the infiltrated density of NK-2567 J-aggregates, in good agreement with that of Ref.[23].

The coupling parameter α can be readily varied in the infiltrated opal by changing the density, N of the infiltrated cyanine molecules. Since the cyanine Rabi frequency splitting, Ω_P is proportional to $\sqrt{\omega_{LT}}$, with $\omega_{LT} \propto N$. By changing N it is actually possible to change the reflectivity spectrum of the infiltrated opal at a fixed angle, since the changing coupling parameter α determine the splitting between the Bragg and polariton reflectivity bands. We use this relation to directly prove the correlation that exists between peaks B_1 and B_2 in the reflectivity spectrum. Figure 0.3 (a) shows the evolution of the infiltrated opal reflectivity spectrum at $\theta = 0$ with the illumination time of a strong incandescent light source, which is used here to bleach the cyanine molecules.

It is seen that peaks B_1 and B_2 approach each other with the illumination time, Figure 0.3(b). At long times both peaks collapse into a single Bragg reflectivity band at about 700 nm (Figure 0.3(a)). This time resolved reflectivity spectrum can be fit (Figure 0.3(b)) using an exponentially decaying density, $N(t) = N(0)e^{\frac{-t}{\tau}}$ with $\tau = 425$ min, and $\alpha(0) = 0.75$. The excellent fit shown in Figure 0.3(b) was achieved when we considered the time dependent dielectric function, $\epsilon_0(t) = 1.5 + 0.16e^{\frac{-t}{\tau}}$; we also used $\omega_B(0) = 742$ nm and $\Delta\omega_B(0) = 31$ nm at $t = 0$. The good agreement between experiment and theory unambiguously shows that the two reflectivity bands are correlated, and therefore the barggoriton approach used here is the correct model.

In conclusion, we showed that a highly polarizable medium that is infiltrated into a PC can induce a transparent spectral region inside the gap when the coupling, or Rabi frequency is strong and the unperturbed polariton frequency is close to the gap frequency.

This is caused due to the strong interaction between the Bragg and exciton-polariton gaps that results in the existence of intra-gap braggoriton excitations, which promote light propagation inside the gap. Although the braggoriton-induced transparency was demonstrated for cyanine dye aggregates infiltrated in an opal PC that does not possess a complete PBG, we expect that our conclusions would also hold in case of a PC with a complete PBG. The induced intra-gap transparency may then serve to direct light traffic in and out of a defect laser resonator inside the PC via a braggoriton type waveguide.

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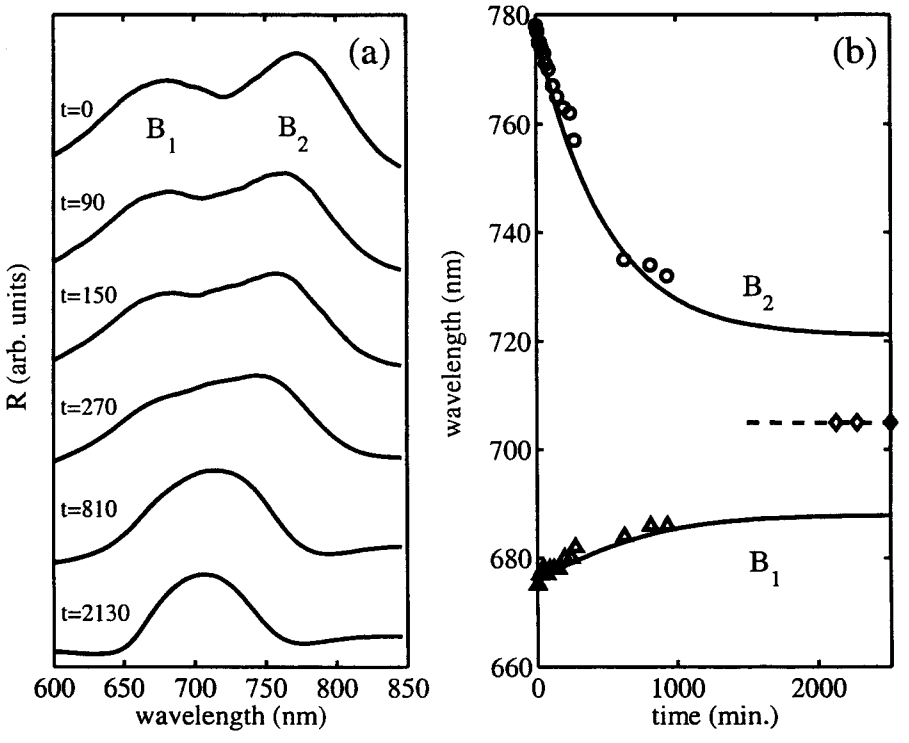

Figure 0.3. The dependence of the reflectivity spectrum of NK-2567 cyanine dye infiltrated into opal measured at $\theta = 0$, on the illuminating time, t in minutes using a strong incandescent light to bleach the dye molecules. (b) The frequency dependence of B_1 and B_2 bands in (a) on the illumination time, t; triangles are for the B_1-branch and circles are for the B_2-branch; the diamond symbols are for the collapsed band at large t, when B_1 and B_2 cannot be separated any more.

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