Angular Redistribution of Spontaneous Emission

We have measured spontaneous emission spectra of laser dyes in strongly photonic crystals, made of inverse opals in titania (TiO$_2$). We have observed that spontaneous emission spectra are strongly modified, and depend on the emission direction relative to the crystal lattice planes. We identify stop bands with large relative widths comparable to the dyes' emission spectra, that strongly attenuate the emission strength. For a wide range of angles, two stop bands appear simultaneously; their angle-dependent frequencies display an avoided crossing that is corroborated by reflectivity experiments. The stop band frequencies agree well with band structure calculations, but differ from simple Bragg diffraction as a result of multiple wave coupling. Strongly reduced dispersion of Bloch modes and multiple wave coupling illustrate mechanisms ultimately responsible for significant changes in the density of states.

3.1 Introduction

As control over spontaneous emission is a primary aim of photonic band gap materials, it is highly relevant to study the radiative properties of light sources inside strongly photonic crystals. Ultimately photonic band gap crystals will not only influence emission spectra, but also emission rates, as the density of states vanishes or changes rapidly. In this regime intricate spontaneous emission dynamics [1–3] are predicted. Even photonic crystals without photonic band gaps, however, can lead to important advances in the control of emission. Recent examples include, e.g., miniature lasers in two-dimensional photonic crystals [4, 5]. Furthermore, it is of prime interest to study the influence of the photonic band structure on emission spectra in the relatively simple frequency range of the lowest order stop gap, before endeavoring to interpret emission spectra for frequencies near a photonic band gap.
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Previous studies of organic dyes [6-9] and semiconductor quantum dots [10-12] embedded inside three-dimensional weakly photonic crystals have revealed modified emission spectra. The luminescence appeared inhibited in particular directions and frequency bands, forming stop bands whose frequencies depend on angle in accordance with Bragg diffraction from a single set of lattice planes. The crystal planes form a Bragg mirror for the luminescence, preventing part of the emission from leaving the crystal along specific directions. No major changes of spontaneous emission lifetimes have been observed, however, because these weakly photonic crystals hardly modified the density of states [13]. These experiments were limited by the low dielectric contrast involved and the concomitant weak interaction with light. The empirically demonstrated [14] minor changes in emission lifetime agree well with the few percent reduction in total solid angle for light propagation due to Bragg diffraction.

Recently developed photonic crystals with high dielectric contrast, known as inverse opals, interact so strongly with light that propagation is inhibited for more than 55% of all directions [15]. Hence, these crystals promise to bring emission experiments in the regime of strong photonic interaction, though insufficient to open a photonic band gap. In this chapter, we study spontaneous emission of laser dyes inside such photonic crystals. We identify a mechanism by which the directional properties of the spectrum are modified. For emission nearly normal to the 111 lattice planes, we observe a single stop band. Over a large angular range, however, we find dual stop bands in the emission spectra, with very large band width. The angular dependencies of the center frequencies of the two stop bands display an avoided crossing. The large angular extent and frequency band width of the avoided crossing demonstrate a multiple Bloch wave coupling phenomenon, which is characteristic for the regime of strong photonicity, and the fundamental ingredient for suppressing the density of states.

3.2 Experiment

The photonic crystals studied here are fcc crystals of close-packed air spheres in a solid matrix of anatase TiO$_2$, prepared by template-assisted assembly [16, 17]. The preparation and structural characterization of these crystals has been reported in Ref. [16, 18], and was performed by L. Bechger and J.E.G.J. Wijnhoven. In brief, fcc opal templates are prepared by drying colloidal crystals that consist of polystyrene latex spheres (Duke Scientific, polydispersity $\leq$ 2%) in water. Such colloidal crystals are formed by sedimentation in a capillary. The artificial opals are infiltrated up to 8 times with a mixture of ethanol and the precursor titanium-(IV) propoxide. After each infiltration step, the precursor is allowed to react with water from the air for one day. After the infiltration steps, the samples are heated up to 450°C in an oven in air. This heat treatment serves the dual purpose of calcining the latex template spheres, and of completing the alkoxydes reaction to crystalline anatase TiO$_2$ as confirmed by X-ray powder diffraction. The volume fraction of solid material comprising these so-called 'inverse opals' or 'air-sphere crystals' ranges from 6 to 12%, depending on the
3.2. Experiment

**Figure 3.1:** (Left) Scanning electron micrograph of a 111 face of an inverse opal with \( a = 480 \text{ nm} \). Dark dots (three per sphere visible) correspond to cylindrical voids connecting this crystal layer to the next layer of air spheres. The scalebar represents 0.5 \( \mu\text{m} \). (Right) Schematic overview of the setup. The pump beam is focused onto the sample face using lens \( L_1 \) (\( f=10 \text{ cm} \)). Luminescence within a cone (apex angle set by aperture \( A_1 \)) centered at a detection angle \( \alpha \) relative to the sample surface normal is imaged onto the spectrometer entrance slit using \( L_1 \) and \( L_2 \) (\( f=12 \text{ cm} \)). A Schott color filter \( F_1 \) prevents scattered laser light from entering the spectrometer. The detection angle \( \alpha \) is varied by rotating the sample. A microscope was used to monitor the pump beam alignment, and the position of the pump spot on the sample.

lattice parameter. Scanning electron microscopy (SEM) images show highly ordered spherical macropores that appear to be faithfully replicated from the opal template, despite an overall shrinkage of \(~ 25\% \). Neighboring air holes are connected by round air channels ('windows') through the titania backbone, which appear as black spots in the SEM pictures, such as displayed in Fig. 3.1(a). These windows correspond to the contact points of latex spheres in the original template. The samples have overall dimensions of the order of millimeters and thicknesses of \(~ 200 \mu\text{m} \). They are composed of high-quality crystal domains with diameters of \(~ 50 \mu\text{m} \), as confirmed by small angle X-ray scattering [18]. Defects, displacements and polydispersity of the air spheres are inherited from the opal template. The internal titania-air interfaces have a roughness of \(< 10 \text{ nm} \), limited by the grain size of titania crystallites. The high dielectric constant of anatase titania (\( \varepsilon = 6.25 \) to 6.5 for visible wavelengths [19]) makes these 'inverse opals' or 'air-sphere crystals' into some of the most strongly photonic crystals available for visible light, with a photonic strength \( \Psi \approx 0.12 \) [15].

In order to study spontaneous emission in these photonic crystals two different organic dyes were used, being Rhodamine 6G (R6G), and Nile Blue (NB) [20]. Crystals with lattice parameters ranging from \( a = 430, 480, 480 \text{ nm} \), doped with R6G, to 480 and 510 nm (NB) were chosen for optimal overlap of the L-gaps with the emission spectra. To incorporate the dye, the air-sphere crystals were immersed in a dilute solution (\(~ 70 \mu\text{mol/l for 24 h in the case of Nile Blue, and } \sim 1 \mu\text{mol/l for 1 h for } R6G) \) of dye in ethanol, to promote the adsorption of dye molecules at the TiO\(_2\)-air interfaces.
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of the voids. Afterwards, the samples were rinsed and dried. It remains challenging to determine the density of dye molecules. From the molar adsorptivity [21] and a crude internal surface area estimate, we expect $\sim 10^2$ dye molecules per air sphere (of radius $\sim 200$ nm). Such a concentration is far below the monolayer coverage density of $\sim 10^5$ chromophores per sphere. The estimate of $10^2$ molecules per sphere may even be an upper bound, given the rinsing cycles after adsorption. The concentration of dye molecules is estimated to be low enough by more than 2 orders of magnitude to avoid reabsorption or energy transfer processes. An upper bound to the critical concentration for reabsorption is determined from the peak in absorption cross-section. Furthermore, our estimate takes due account of the extended path length photons traverse inside the samples due to random scattering.

To ensure that solely emission is recorded from internal sources, well within the bulk of the crystal, the dye adsorbed near the external sample surface was selectively bleached [9]. Bleaching of the dye was limited to the first few crystal layers by illuminating the photonic crystals with an intense laser beam (488 (R6G) or 514 nm (NB)) impinging at the Bragg angle. At this angle the pump intensity decreases exponentially with depth into the sample. Spectra were found to be independent of observation angle prior to bleaching. Bleaching caused angle-dependent modifications of the spectral lineshapes to occur. The crystal layers close to the external crystal-air interface were bleached until modification of the lineshapes stopped. Further bleaching only resulted in a decrease of the emission intensity.

A schematic overview of the optical setup used to measure emission spectra is shown in Fig. 3.1. Depending on the dye, the 488 nm (R6G) or 514 nm emission of an Ar-ion laser was used to excite the dye. The $p$-polarized pump beam was incident on the samples at angles away from the Bragg condition for the pump frequency. The pump beam was focused to a spot $\sim 30 \mu$m in diameter on the sample surface using a 10 cm focal length lens. The samples were glued to needle-tips and mounted in a goniometer, to acquire emission spectra as a function of the detection angle $\alpha$ relative to the surface normal, which corresponds to the 111 reciprocal lattice vector. The angle of incidence of the pump beam also changed with the sample orientation, although the illuminated spot remained the same. At $\alpha = 0^\circ$, the incident angle of the pump beam amounted to $\sim 30^\circ$. For increasing $\alpha$, the surface normal of the sample was rotated towards the pump beam. The alignment of the laser beam on the sample and the rotation axis of the goniometer was monitored through a long working distance microscope. Emission within a cone of $5^\circ$ around the detection angle $\alpha$ was imaged onto the entrance slit of an Oriel MS-257 0.25 m, f/4 grating spectrometer (in the case of Nile Blue), resp. a Carl Leiss\(^1\) prism spectrometer (R6G), which was calibrated using the emission lines of a Neon lamp. The $p$-polarized component of the emission was selectively probed, either due to spectrometer grating efficiencies, or by using a polarizer in the case of the R6G measurements. In both instances, the resolution amounted to $\sim 100$ cm$^{-1}$. A Hamamatsu R3809U Micro Channel Plate detector was used to record the fluorescence. The spectra have been corrected for detector dark

\(^1\)Carl Leiss GmbH Berlin, as opposed to Carl Zeiss.
### 3.3 Emission spectra and stop bands

Emission spectra at select detection angles of Nile Blue in a crystal with $a = 510$ nm, and of R6G in a crystal with $a = 480$ nm are presented in Fig. 3.2(a) resp. (c). For detection angles larger than 60°, the spectral line shapes of the emission remain unchanged, and the high frequency edge of the emission spectra has the same shape as observed at low detection angles, between $\alpha = 0^\circ$ and 25°. This implies that at angles larger than 60° the stop band does not overlap the emission spectrum of the dye, both in the case of Nile Blue and R6G. In comparison, at $\alpha = 0^\circ$ the photonic crystal with $a = 510$ nm greatly suppresses the emission of Nile Blue in the spectral range from 14000 to 16200 cm$^{-1}$. With increasing detection angle the low-frequency components of the emission recover, and the frequency range in which emission is suppressed shifts to higher frequencies, as expected from Bragg’s law for a photonic crystal stop.

#### Figure 3.2: Normalized emission spectra as a function of frequency for Nile Blue (a) resp. R6G (c) in titania inverse opal with lattice spacings $a = 510$ nm resp. 480 nm. Bottom panels (b) and (d) show the corresponding relative intensities obtained from the spectra in (a) and (c). Black curves are obtained at $\alpha = 0^\circ$, grey dashed curves at 25° (a,b) resp. 15° (c,d), black dashed at 45° (a,b) resp 30° (c,d), and solid grey curves at 60°. Reflectivity data in (b) are shown for $\alpha = 0^\circ$ (black dash-dotted) and 30° (black dotted curves). Double stop bands at 25° and 45° are indicated by arrows in (b). Fitted double Gaussians are indicated by thin grey dotted lines for $\alpha = 25^\circ$. Count, and the measured intensities of spectra at various angles have been adjusted to overlay their low- or high frequency ranges. In these frequency ranges no crystal effects are observed to modify the spectra.
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Figure 3.3: Central wavelength $\lambda_B$ (in air) versus lattice parameter $a$ of the first order Bragg diffraction by 111 lattice planes of titania inverse opals. Open diamonds correspond to stop bands in emission (Chapters 3 and 4). Closed circles correspond to stop gaps in diffuse transmission (Chapter 7). The closed triangle (Chapter 6) and open diamond (Chapter 4) at $a = 350$ nm were determined from reflectivity. The solid line is Bragg's law, assuming an effective refractive index $n_e = 1.15$ (consistent with TiO$_2$ volume fractions between 6% ($n_e$ from averaged $e$) and 10% ($n_e$ from averaged $n$)). Lattice parameters were determined from SEM images. Symbol sizes are comparable to the error in $a$.

gap from a single set of lattice planes. The same observations hold for the emission spectra of R6G in the sample with $a = 480$ nm, although the suppression bands are blue shifted. At $\alpha = 0^\circ$ for instance, the suppression is shifted to the range from 15000 to 17000 cm$^{-1}$, in accordance with the reduced lattice parameter (see Figure 3.3). For both dyes we verified that the emitted intensity is proportional to the pump power, and that the line shapes are independent of the pump intensity. As expected based on the low dye doping concentration, these observations show that lasing and amplified spontaneous emission effects can be excluded. By traversing sample faces with the pump beam focus, we were able to map the angle-resolved spectral line shapes as a function of position on the sample, with a resolution of 50 $\mu$m. The spectral line shapes are well reproduced over sample areas up to 0.8 mm in diameter. In general, the angle-dependent modifications of the spectral line shapes as shown in Fig. 3.2(a) and (c) occur on those regions of photonic crystal samples which show bright opalescence. On the other hand, spectra from parts of photonic crystals which did not show clear opalescence, also did not show a clear angle-dependence. The angle-dependent modification was observed both in experiments with Nile Blue and with R6G. The blue shift of the stop band center frequencies at $\alpha = 0^\circ$ with decreasing lattice parameter is demonstrated in Fig. 3.3. We find stop band center frequencies 14800 cm$^{-1}$, 15500 cm$^{-1}$, 15600 cm$^{-1}$ and 17200 cm$^{-1}$ respectively, for $a = 510, 480$ nm (NB) and 480, 430 nm (R6G). Both the blueshift of the $\alpha = 0^\circ$ stop band with decreasing lattice parameter, and the reproducibility of the experiment with different dyes indicate that the observed features are indeed a photonic crystal effect.
To determine the directionally dependent photonic stop band effect on the emission spectra, one would like to determine a 'transfer function' that depends solely on the photonic crystal, and not on the choice of dye. Such a transfer function can be found by dividing the angle-dependent fluorescence spectra by a suitable reference. A priori, the spectra are determined by (i) directional redistribution due to stop gaps (as observed), (ii) the (local) photonic density states sampled by the sources and (iii) the inhomogeneous broadening of the dye, which is partly determined by chemical interactions with the substrate. As dye molecules effectively act as four level systems, lineshapes in different photonic systems can be compared without taking into account the pump light distribution, as long as the pump wavelength is the same. To focus purely on the directionally dependent modifications, the reference spectrum should originate from a system with the same chemical and optical environment of the light sources. The reference of choice is therefore the angle-integrated emission spectrum of the dye in the specific sample under consideration. As quantitatively motivated both empirically and theoretically in Chapter 7, the spectrum observed for $\alpha \geq 60^\circ$ is a good measure of the angle-integrated spectrum over most of the spectral range. This is due to the fact that no photonic stop gap overlaps the emission spectra for detection angles in excess of 60°. Dividing the $\alpha = 0^\circ$ lineshape by the $\alpha = 60^\circ$ spectrum, a stop band centered at $14800 \text{ cm}^{-1}$ for $a = 510 \text{ nm}$ (Nile Blue) and $15600 \text{ cm}^{-1}$ for $a = 480 \text{ nm}$ (R6G) is indeed obtained. The analysis may be slightly improved by noting that dividing a spectrum at angle $\alpha_1$ by a spectrum at $\alpha_2$ with negligible stop band overlap gives the stop band at $\alpha_1$ if the ratio is less than unity. The stop band at $\alpha_2$ is found from the inverse ratio. The analysis is more complicated if the transfer functions themselves exceed unity (Fig. 3.2(d), see Chapter 7), and if the ratio is taken of spectra with partially overlapping stop gaps. By careful analysis we were able to correct the $\alpha = 60^\circ$ spectrum for a residual stop band at very high frequency ($> 18500 \text{ cm}^{-1}$ for $a = 510 \text{ nm}$, resp. $19300 \text{ cm}^{-1}$ for $a = 480 \text{ nm}$). The lineshape ratios for different samples and dyes are largely sample-independent, hence the stop bands are unambiguously determined.

Using the corrected $\alpha = 60^\circ$ spectrum, we have extracted stop bands for all detection angles, a selection of which is shown in Fig. 3.2(b) for Nile Blue, and (d) for R6G. At emission angles close to $\alpha = 0^\circ$, single broad stop bands appear. It is apparent that the relative width of the stop band $\Delta \omega/\omega = 10$ to 15% is so broad, that it is comparable to the broad spectral range of the organic dyes. The large stop band width is a signature of strong photonic interaction. At larger detection angles, a transition to a double stop band appears. The stop band edge frequencies will be discussed in Section 3.5. For frequencies within a stop band, the emission is reduced by $\sim 50$ to 75%. Apart from stop bands, the $\alpha = 0^\circ$ data in Fig. 3.2(d) show a slight enhancement compared to the $60^\circ$ spectrum in a frequency window to the blue of the L-gap. This enhancement will be explained in Section 7.4. Figures 3.2(b) and (d) clearly demonstrate that photonic stop gaps impose a strong attenuation on the transfer of radiant energy to free space. We explain the magnitude of the attenuation in Section 3.4.
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![Diagram of light transport and internal diffraction](image)

**Figure 3.4:** (Sketch) Each individual source has a position dependent radiation pattern, determined by the Bloch modes available at the source position. Directional properties of each source are washed out by multiple scattering over length scales \( \ell \). Near the external interface the crystal planes internally diffract the diffuse luminescence, giving rise to stop bands in the spectra. The relevant length scale for internal diffraction is \( L_B \).

### 3.4 Diffuse transport and the stop band attenuation

For light sources embedded in a perfect crystal, one would expect that no emission into stop gap directions is possible. A perfect crystal should therefore give rise to a complete vanishing of the fluorescence intensity in stop gap directions. Instead, we observe an attenuation of 50% to 75% at \( \alpha = 0^\circ \) for all crystals studied. Limited attenuation of emission in stop band directions has previously been observed in the case of weakly photonic crystals [6–12]. For such near index-matched photonic crystals, the limited attenuation has been identified as being due to single scattering by intrinsic defects near the sample surface [9]. In the present case, the mechanism appears related, as it can also be attributed to random scattering. In weakly photonic samples the mean free path \( \ell \) typical for random scattering exceeds the sample dimensions. In contrast, transport of light in the titania inverse opals is diffuse\(^2\) on length scales \( \ell \sim 15 \, \mu\text{m} \) smaller than the sample thickness \( L \sim 200 \, \mu\text{m} \). In brief, one should take into account that fluorescence emitted by a light source inside the bulk of the crystal does not reach the detector directly, but undergoes a series of scattering events, as sketched in Fig. 3.4. Even though different sources can have different radiation patterns, owing to their different local photonic environment, none of these directional properties of each source inside the photonic crystal reaches the observer. Instead, emission from all sources propagates diffusively to the crystal interface. Diffuse light emanating from a depth \( z < \ell \) less than the mean free path from the surface propagates ballistically to the crystal-air interface, but may be redirected to the detector by some scattering event less than \( \ell \) from the surface (see Fig. 3.4). The mean free path \( \ell \) is larger than the exponential attenuation length \( L_B \) associated with Bragg diffraction.

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\(^2\)An introduction to diffusion theory, and experiments to determine the transport mean free path \( \ell \) as well as explanations of the source of random multiple scattering are the subject of Chapter 6. The interplay of internal Bragg diffraction and diffusion of light has been investigated in the experiments reported in Chapter 7.
3.4. Diffuse transport and the stop band attenuation

**Figure 3.5:** (Left) Calculated energy density of the diffuse pump light for a sample of 200 μm thickness, a mean free path of 15 μm and a pump beam of waist $w = 30$ μm. Assumptions of the calculation are described in the text. Pump light is spread out over a large volume of $65 \times 40$ μm at a mean depth of 50 μm. Within this volume the diffuse energy density exceeds the energy density of the ballistic beam (right) by a factor $\sim 4$. (typically $L_B/\ell \sim 0.2–0.5$). Hence, intensity scattered at a distance $z < L_B$ less than the Bragg attenuation length from the interface is hardly Bragg diffracted. On the other hand the remaining fraction $1 - L_B/\ell$ for which the last scattering event occurs in the range $L_B < z < \ell$ propagates a sufficient distance to develop a stop band due to internal Bragg diffraction. This crude model predicts a total attenuation in the stop band equal to $1 - L_B/\ell = 50\%$ to $80\%$, in agreement with the experiment.

The pump light distribution is also affected by random multiple scattering. The diffusion approach therefore gives an adequate description of the spatial dependence of the pump light energy density within the sample, on length scales comparable to or bigger than the mean free path. In order to determine the size and depth of the sample volume in which dye molecules are excited by the pump light, we examine the solution of the stationary diffusion equation

$$D \nabla^2 W_D = \frac{I(r)}{\ell}$$

(3.1)

for the diffuse pump light energy density $W_D$, with diffusion coefficient $D = 1/3c\ell$ and boundary conditions as explained in Chapter 6. The source term in the diffusion equation is determined by the incident intensity distribution

$$I(r, z) = I_0 e^{-r^2/(2w^2)} e^{-z/\ell},$$

(3.2)

where $z$ denotes the depth into the sample, and $r$ the distance from the axis of the incident beam. The Gaussian incident beam with peak intensity $I_0$ decays exponentially with depth into the sample due to extinction according to Lambert-Beer’s law.
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In correspondence with the experiment, we consider a slab of thickness \( L = 200 \, \mu m \) that is infinite in the lateral directions, and a pump beam waist size \( w = 30 \, \mu m \). We take a mean free path \( \ell = 15 \, \mu m \), in accordance with the experiments presented in Chapter 6.

We find a diffuse pump light energy density \( W_D \) extending over a volume several mean free paths across, as displayed in Fig. 3.5(a). On the \( r = 0 \) axis collinear with the input beam, the mean depth \( \langle z \rangle = \int z W_D(z) dz / \int W_D(z) dz \) at which dye molecules are excited amounts to \( \approx 50 \, \mu m \). The mean injection depth increases with increasing waist \( w \) to a maximum of order \( \sim L/3 \) (for \( L \gg \ell \)). As a measure of the spatial extent of the diffusely pumped volume, we propose \( \sqrt{\langle r^2 \rangle} \) at mean injection depth, amounting to \( \sim 65 \, \mu m \) in the radial direction, and \( \sqrt{\langle z^2 \rangle - \langle z \rangle^2} \approx 40 \, \mu m \) along the sample normal. To obtain the total energy density within the sample, one should add the contribution of the exponentially attenuated incident beam (so-called ‘coherent beam’) to the diffuse energy density, which is plotted in the separate panel Fig. 3.5(b). Naturally, the contribution \( W_I \) of the coherent beam is confined to a much smaller volume, i.e., one mean free path from the surface, with a lateral extent equal to the beam waist. More strikingly, the maximum energy density of the coherent beam (at the sample surface) is lower than the maximum energy density of the diffuse light (at \( z \sim 2\ell \)) by approximately a factor 4. This result indicates, as expected, that random multiple scattering increases the average path length that pump light traverses in the medium, thus enhancing the pump efficiency. In conclusion, diffuse transport of light is crucial in determining (i) the pump light distribution, and (ii) the attenuation of emission in stop band directions.

3.5 Stop bands beyond simple Bragg diffraction

At low emission angles close to normal to the 111 lattice planes, single broad stop bands appear in Fig. 3.2(b) and (d). Interestingly, at larger detection angles \( \alpha \geq 25^\circ \), a transition to a double stop band appears. As a typical example, we focus on Fig. 3.2(b). To clarify the double-stop band structure, which appears partly obscured due to the large width of the stop bands compared to the frequency separation, we have indicated the center frequencies of the stop bands with arrows. We denote the low-frequency stop bands by \( S_1 \), and the higher frequency stop band by \( S_2 \). With increasing angle, the higher frequency stop band \( S_2 \) becomes more apparent, while \( S_1 \) decreases in amplitude. The stop band spectrum at \( \alpha = 45^\circ \) shows evidence of a weak \( S_1 \) feature at 17000 cm\(^{-1}\) and a clear \( S_2 \) band at 18700 cm\(^{-1}\). For \( \alpha = 60^\circ \), no more evidence of the \( S_1 \) band is found, and the low-frequency edge of the \( S_2 \) band has shifted beyond 18500 cm\(^{-1}\) (black horizontal arrow), leaving the emission spectrum essentially unsuppressed. Neither the occurrence of double stop bands, nor their frequency dependence can be explained as simple Bragg diffraction from a single set of lattice planes, but are likely due to a coupled wave phenomenon.

To confirm that the stop bands in emission of internal sources indeed correspond to the photonic band structure, additional reflectivity measurements were performed.
3.5. Stop bands beyond simple Bragg diffraction

The reflectivity was determined using externally incident plane waves from a white light source in conjunction with a Fourier-transform spectrometer, as described in Ref. [15, 22]. Reflectivity experiments readily reveal the center frequencies and widths of stop bands. To allow for a direct comparison of the reflectivity bands with stop bands in emission, reflectivity data $R(\omega)$ are scaled onto the emission stop bands as $1 - \beta R(\omega)$. The scaling constant $\beta$ accounts for the difference between peak reflectivity and attenuation at the center of the stop band. The peak reflectivity of $\sim 20\%$ is limited by mosaic spread and grain boundaries occurring on a length scale of $\sim 50\, \mu m$, much smaller than the probe beam diameter $\sim 500\, \mu m$. Representative reflectivity results for $\alpha = 0^\circ$ and $45^\circ$ are shown in Fig. 3.2(b). As expected, a single stop band is revealed at a reflection angle $\alpha = 0^\circ$, and a much broader double reflection band appears at $\alpha = 45^\circ$, in agreement with the emission data. Although minor differences between reflectivity and emission data remain, there is good agreement between the single- and double stop bands in emission and in reflectivity. This confirms that the avoided crossing observed in the emission spectra is caused by the photonic band structure.

To quantify the dispersion of both stop bands $S_1$ and $S_2$, we have extracted the upper and lower frequency edges of the stop bands for all detection angles, as shown in Figure 3.6 for a typical example. Here, we have defined the stop band edges as the frequencies at half minimum of an attenuation band. An ideal diffraction peak would have a flat top with 100% reflectivity or attenuation, that abruptly falls off at the edges. Extinction causes a rounding of stop bands, and reduces the maximum reflectivity, or attenuation. In the absence of broadening mechanisms such as crystal
strain, the edges at half maximum (resp. minimum) of reflectivity or emission bands still represent a reliable though heuristic measure of the widths of stop gaps in the dispersion relation [23, 24]. Central frequencies and stop band edges were extracted by fitting double Gaussian peak shapes to the data in Figure 3.2(b). The number of adjustable parameters was limited by assuming both Gaussians to have equal frequency widths. An example of such a fit is indicated by the two thin grey dotted lines in Figure 3.2(b). The stop band edges of both stop gaps can be determined unambiguously from the two-Gaussian fit. For small angles $\alpha \leq 30^\circ$, the center frequency of stop band $S_1$ closely follows the frequency dependence expected for simple Bragg diffraction, corresponding to the dotted line indicated in Fig. 3.6. Near $\alpha = 30^\circ$, there is a marked departure from simple Bragg diffraction, characterized by (i) the appearance of the high frequency stop band $S_2$, and (ii) the fact that the $S_1$ center frequency remains at frequencies lower than Bragg’s law predicts. The two bands display an avoided crossing centered at $\sim 17000$ cm$^{-1}$ over a large angular range.

### 3.6 Geometry of the avoided crossing in the Brillouin zone

The avoided crossing phenomenon evident in stop gaps in emission has previously been observed in reflectivity experiments on similar samples [22]. Essentially, the internal Bragg diffraction phenomenon giving rise to the stop gap at larger diffraction angle is not solely determined by the 111 lattice planes, but also by the family of 200 lattice planes. It is important to note that the avoided crossing does not appear between just two dispersion branches, but that three reciprocal lattice vectors are involved. To illustrate the physics, we consider a cross-section of the first Brillouin zone through the $\Gamma, U, L, K$ points, as sketched in Fig. 3.7. The stop gap associated with simple Bragg diffraction by the 111 crystal planes appears when the wave vector $k$ touches the hexagonal facet of the first Brillouin zone. In this case $k$ is strongly coupled to its Bragg diffracted counterpart $k' = k + G_{111}$, on the opposite face of the Brillouin zone. The $L$-gap corresponds to an internal propagation angle $\alpha' = 0$, with wave vector $k$ pointing from $\Gamma$ to $L$. The stop gap associated with 111 diffraction for larger angle $\alpha'$ can be traced by scanning the tip of the wave vector $k$ along the $LU$-line, away from the ($-L$-point. At some point the wave vector passes the $-U$ point and moves into the second Brillouin zone. At the angles $\alpha'$ where $k$ is close to the $-U$ point, the plane wave with wave vector $k$ not only couples to $k' = k + G_{111}$, but also to the 200 diffracted $k'' = k' + G_{200}$. In a Bragg diffraction experiment this implies that, given the incident wave vector $k_{\text{in}} = k$, two diffracted wave vectors appear simultaneously inside the crystal, e.g., $k'$ and $k''$. The dispersion relation, and diffraction efficiencies, are determined by the coupling between all three waves (or six, to account for polarization), and can not be described by the crossing of two separate stop gaps determined by simple Bragg diffractions. Instead, the electromagnetic waves organize into normal modes in which the $G = 000, 111$ and 200 components

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3The $L$-gap itself can be understood as an avoided crossing between two dispersion branches involving $G = 000$ and $G = 111$, as evident in the repeated zone scheme in Fig. 1.1.
3.7. Band structure

To investigate the angle-dependent features of the dispersion relation and to arrive at a quantitative comparison with the stop band edges in Fig. 3.6, we have calculated the plane-wave band structure. The position dependent dielectric function $\varepsilon(r)$ assumed here, is based on experimental observations of the structure of the crystals [16, 18]. For the model we assume close-packed air spheres (radius $r = a/\sqrt{8}$) covered by overlapping shells of solid material ($\varepsilon = 6.5$) of outer radius 1.09$r$, and connected by cylindrical windows of radius 0.4$r$ connecting neighboring air spheres. The shell thickness and window size are compatible with SEM observations, and correspond to a volume fraction of $\sim 10.7\%$ titania, consistent with available data [18]. The three anticrossing bands in the resulting band structure for the relevant polarization are shown in Fig. 3.6. The full band structure agrees with reflectivity features both in the regime of first order and second order Bragg diffraction [22, 25]. Internal wave vectors were converted to external propagation angle by applying parallel momentum conservation at the crystal-air interface. The two curves starting at $\alpha = 0^\circ$ correspond to
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eigenfrequencies of the mixed 000 and 111 modes, and delimit the 111 Bragg diffraction stop band edges. It is clear that the calculated mode frequencies agree well with the $S_1$ stop band edges derived from the emission spectra. The intermediate and high frequency modes agree well with the edges of the $S_2$ stop band. Though these dispersion curves were calculated using 725 plane waves, the same qualitative behavior is apparent in a model employing only the $G = 000, 111$ and 200 (and symmetry related) reciprocal lattice vectors [22]. This indicates that the observed avoided crossing is due to the 200 Bloch mode that couples with the 000 and 111 modes.

3.8 Conclusion

We have studied the angular distribution of spontaneous emission of dyes in strongly photonic inverse opals. We have found wide stop bands that strongly attenuate the transfer of radiant energy to free space. For the first time we find a double stop band in emission spectra. The angular dependence of the center frequencies of the two stop bands show an avoided crossing over a large angular and frequency range. The avoided crossing is determined by multiple Bragg wave coupling of 000, 111 and 200 modes, and is well understood in terms of the photonic band structure. In the range of the avoided crossing the modes become nearly dispersionless. Flattening of dispersion relations due to band repulsions is the hallmark of strong multiple wave coupling phenomena that will ultimately result in a photonic band gap. Depending on the range of solid angle over which the avoided crossing occurs, a significant modification of the density of states can be expected. Experiments to probe the density of states are the subject of Chapter 4. Furthermore, we conclude that random multiple scattering due to structural disorder plays a key role in the transport of luminescence and pump light.

References


