Blue phases of cholesteric liquid crystals as thermotropic photonic crystals

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(Received 6 January 2000)

The study of dye-doped low pitch cholesteric liquid crystals in their blue phases as an example of tunable "weak" photonic crystals is proposed and demonstrated. The presence of the blue phases in cholesterics can be tuned with temperature, and this allows for an easy *in situ* comparison of the emission and/or absorption of the dyes with or without an enwrapping lattice of disclination lines. The fluorescence emission of the dyes is shown to be affected by the presence of the blue phases. Although unlikely to be suitable for real applications (due to the natural low refractive index contrast), these systems may represent unique examples of tunable photonic crystals. It is proposed that single crystals of dye-doped blue phases should provide a very interesting testing ground for the study of optical emission anisotropies which can, on the other hand, be controlled by an external parameter.

PACS number(s): 42.70.Qs, 42.70.Df, 61.30.Jf

The idea of controlling the spontaneous emission of atoms and molecules by means of a modification in the photon density of states (DOS) was put forward more than ten years ago in the pioneering work of Yablonovich [1], and the denomination photonic crystals was coined to identify those structures that alter the otherwise isotropic distribution of electromagnetic modes in vacuum. The vast majority of examples achieve a modification in the photonic DOS by virtue of a spatially dependent dielectric function $\epsilon(\vec{r})$, which plays a role similar to that of the position dependent atomic potential $V(\vec{r})$ in the electronic structure of matter (except for the fact that electromagnetic waves are a vectorial field, while electrons are scalar waves). If $\epsilon(\vec{r})$ is periodic, the full power of the Bloch theorem can be applied, and the electromagnetic band structure can be obtained. This sometimes results in the presence of gaps which are opened at the Brillouin zone boundaries. In analogy with other elementary excitations in solids, a rule of thumb is that the electromagnetic wavelength λ should be of the order of the lattice spacing a in order to see a standing wave interference (Bragg reflection) and the presence of forbidden energies. For this reason, most of the original work was performed in the microwave region, whereas λ is of the order of macroscopic objects and, therefore, three-dimensional periodic lattices could be built by drilling holes into large bulk dielectrics [2].

A great deal of work was devoted to photonic crystals in the last few years. Among other things, the search for structures which would display forbidden energy gaps for arbitrary polarizations and incident wave vectors (stop bands) [3], the possibility of observing electromagnetic localization in disordered dielectrics [4], and the presence of defectinduced donor or acceptor states in the gap (as in semiconductors) [5] are a few examples of the vast range of problems that have been studied in this field [6]. It was realized from the very beginning [1] that photonic crystals in the visible range will have dramatic consequences on the optical proplattice, and that this could be used for controlling the spontaneous emission or absorption with a myriad of potential useful applications, not only for spectroscopic studies of atomic or molecular short lived excited states, but also to achieve population inversion in solid-state lasers. However, the quest to extend the general principles of photonic crystals to the visible range was hitherto challenged by several experimental problems. One-dimensional (1D) photonic crystals in the infrared range ($\lambda \sim 1 \mu m$) are readily obtained through distributed Bragg reflectors in semicondutor microcavities grown by molecular beam epitaxy [7]. Single crystals of cholesteric phases with parallel alignment also belong to this group; forbidden energies appear for circularly polarized light in specific frequency ranges for propagation along the helix. Two- and three-dimensional extensions in the visible are normally much more difficult to obtain. One useful strategy has been the search for materials that would selfassemble into photonic crystals. In the 3D case, a very important role was played by opal and dye-polymer-opal composites [8]. Very recently, the modification of the spontaneous emission of dyes in a 3D self-assembled opal photonic crystal with a stop band in the visible has been demonstrated [9]. Two crucial parameters for the existence of a stop band in a lattice formed by two components (with dielectric constants ϵ_1 and ϵ_2 , respectively) are the *dielectric* contrast $\delta = 2|\epsilon_1 - \epsilon_2|/(\epsilon_1 + \epsilon_2)$, and the specific geometry of the lattice. For a given lattice, larger δ 's increase the likelihood of forming a stop band.

erties of atomic and/or molecular species embedded in the

In the completely unrelated field of liquid crystals (LC's), on the other hand, the existence of lattices of disclinations, the so called blue phases (BP's), has been known for quite some time in low pitch cholesterics [10]. The blue phases come into existence within a narrow temperature range $(\sim 1-2^{\circ}C)$ at the transition between the isotropic (I) and cholesteric (Ch) phases [11], and they normally display both thermal hysteresis and supercooling. This latter property means that there is a latent heat associated with their formation, and this implies the presence of a first-order phase transition. Although their existence has been known for quite

1435

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some time, it is relatively recently that they have been recognized as thermodinamically distinct and stable phases. BP's arise through a delicate interplay between the bulk and gradient free energies, and have been called crystalline liquids as opposed to liquid crystals. A comprehensive account of their physical properties and a review of the early work in the field can be found in Ref. [12]. Except for a phase called blue fog (BPIII) [13], which apparently has a glasslike or quasicrystalline structure and appears only in some compounds, the two most frequently encountered BP's are BPI and BPII [12] which have a cubic structure. It was shown that the helical arrangement of molecules in the Ch phase cannot be deformed continuously into a cubic lattice without generating defects. The blue phases BPI and BPII are, therefore, seemingly unique cases of natural occurring 3D regular lattices of disclinations (defects). A typical lattice spacing for the array of disclinations in most cholesterics is in the visible range. Accordingly, BP's disperse visible light quite effectively in the same way that x rays would be dispersed in a typical crystal lattice. The early reports were done on cholesterics with BP's that scattered light quite strongly in the blue. Nowadays, however, there are known examples of mixtures with BP's which scatter light in the green, yellow, or red, thus allowing for some tunability according to chemical composition.

Finally, the field of dye-doped LC's has received considerable interest in the last few years. Dye-doped LC's display unusual nonlinear optical phenomena which were used to achieve enhanced optical torques [14], high-resolution optical recording [15], and light-induced director reorientations to write permanent holographic gratings [16], among other phenomena. Dye-doped cholesterics in their BP's, on the other hand, have not yet been extensively studied.

In this Brief Report, we show evidence that BP's affect the fluorescence emission of diluted dyes within the sample. The principal drawback in terms of a photonic crystal effect is the fact that the *dielectric contrast* for a lattice of disclinations is rather weak and, accordingly, the existence of a stop band for arbitrary wave vectors and polarization within an energy range is unlikely. Moreover, the lattices cannot be arbitrarily chosen, but are rather dictated by the intrinsic geometrical nature of the BP's. Nevertheless, the beauty of their study resides in the fact that the presence of a particular BP can be tuned with temperature (allowing for an easy in situ comparison of the emissions with or without the "photonic crystal"), and that it is possible to obtain single crystals of these structures, thus making them interesting form a fundamental point of view. Strictly speaking, they can be considered as self-assembled 3D weak photonic crystals which can be tuned by temperature.

Figure 1(a) shows the transmission of an unpolarized Xe lamp (normalized to the transmission in the isotropic phase) of an undoped cholesteryl oleyl carbonate sample in the BPI phase at room temperature (RT) with a cell thickness of 100 μ m. This sample shows considerable supercooling of the BP's at RT (~5°C) and it is partly oriented within the cell. The data interpretation follows precisely that of Meiboom and Sammoy [13,17]; i.e., for an unoriented sample, Bragg reflection becomes possible if the wavelength λ of light satisfies the condition $\lambda \leq 2n(\lambda)d_{h,k,l}$, where $n(\lambda)$ is the index of refraction, and $d_{h,k,l}$ the spacing among the



FIG. 1. (a) Transmission and right-angle dispersion of the sample in the BPI phase. Both measurements are normalized to their corresponding spectra in the I phase. (b) Normalized fluorescence emission in the forward direction (with respect to the excitation) of a dye-doped sample under the same experimental conditions in (a). Note the presence of a *dip* (\sim 3%) in the energy range where the sample Bragg scatters light. See the text for further details.

(h,k,l) crystal planes. For decreasing λ 's, the transmission spectra will show steps (which may also look like dips depending on the degree of order of the sample [13,17] for those wavelengths where the aforementioned condition is satisfied. It is assumed throughout that the cubic BPI phase does not alter the polarization state of the light. The *dip* at \sim 450 nm is assigned to the (200) Bragg scattering condition according to similar data on other cholesterics. Under white-light illumination, the sample looks blue to the naked eye, and this can be quantitatively measured if the scattered light at 90° (from the direction of propagation of the light beam) is measured and normalized to the residual scattering at 90° in the I phase. This is also displayed in Fig. 1(a), and confirms the fact that the sample scatters light around 450 nm in its BPI phase. Figure 1(b) shows the normalized (to the spectrum in the I phase) forward fluorescence emission of a 10^{-3} -mg/ml dye-doped sample in the BPI phase. Any dye with fluorescence in this energy range will show the same effect, we show in this particular case that of a laser dye which is typically pumped in the ultraviolet by a yttrium aluminum garnet laser with a tripler in a tunable dye laser. It is quite clear from Fig. 1(b) that a dip in the normalized forward emission appears precisely where the BPI phase scatters light most effectively. In other words, the emission of the dyes *feels* the presence of the lattice of disclinations. This result is completely equivalent to the emission suppression observed in dye-doped opal samples, except for the fact that the sample is polycrystalline in this case. It is worth noting that if the dyes were excited by an isotropic pump, there would be no decrease in the fluorescence emission along a particular direction. The sample would still Bragg scatter light due to the presence of the BP's, but scattering processes in different directions would compensate for one another and cancel out. The fact that the pump beam is along a specific direction with a given polarization, however, sets in a priviledged direction and an asymmetry in the excitation. In particular, those dyes which have their transition

dipole moment perpendicular to the incident polarization will not be excited by the pump beam. The fluorescence in the forward direction will be Bragg scattered by the presence of the BP's, and these scattering processes are not compensated for, thus allowing for the observation of a net decrease in the emission even when the sample is polycrystalline. A similar situation would arise with x rays. Imagine that we have an isotropic source of x rays within a polycrystalline sample. Even though Bragg-scattering processes exist, we would not be able to see anisotropies in the emission because different directions will compensate for one another and no crystallographic information will be gained. The fact that we can obtain information from a powder through the effect of the crystal lattice on the x rays in a typical experiment is because the incoming beam fixes a preferential direction. In the case of dyes, the preferential direction is fixed by incoming polarization of the pump beam. The data in Fig. 1(b) clearly demonstrate that BP's affect the emission of the dyes, although the effect is small in comparision with typical suppressions in, for example, opal. We regard this simple result, however, as an indication that photonic crystal effects can be seen in cholesterics that display BP's, and this should be an interesting boost for the study of BP's single crystals which should provide further insights into the emission anisotropies within these remarkable states of matter. Further work in dye-doped BP's single crystals observed by optical microscopy is in progress, and will be reported elsewhere [18].

It is finally interesting to see how the same ideas of temperature tuning, LC's, and photonic crystals, have been used in a completely different manner in Ref. [19] where the transmission spectra of LC-infiltrated synthetic opal was measured and shown to display a "tunable" stop band as a function of temperature. A photonic defect mode in a cholesteric LC was also recently reported [20]. It may very well be that LC's have much to contribute in the field of photonic crystals, either as host materials with tunable optical properties, or through their intrinsic phases with nontrivial topologies like BP's.

In closing, we showed evidence which indicates that cholesteric LC's may be used as *thermotropic photonic crystals*. It would be very interesting in our opinion to calculate the photonic band structure of some of the arrays of disclinations present in the BP's [12], and predict the emission anisotropies along crystalline faces which are observable in real experiments. These calculations have not yet been performed, to the very best of our knowledge, and they should provide very challenging examples of photonic band structures. In particular, in terms of the role played by the optical activity of the molecules and the Ch phase, which is an added issue with respect to conventional photonic band structure calculations with isotropic dielectrics and seems to be compensated for in the cubic structures characteristics of the BP's.

Useful discussions with M. Nöllmann and J. Seddon are gratefully acknowledged.

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