Photonic Band Structure of fcc Colloidal Crystals

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Polystyrene colloidal crystals form three dimensional periodic dielectric structures which can be used for photonic band structure measurements in the visible regime. From transmission measurements the photonic band structure of an fcc crystal has been obtained along the directions between the *L* point and the *W* point. Kossel line patterns were used for locating the symmetry points of the lattice for exact positioning and orientation of the crystals. In addition, these patterns reveal the underlying photonic band structure of the crystals in a qualitative way.

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For the last eight years, the analogy between the propagation of electromagnetic waves in periodic dielectric structures, dubbed photonic band gap (PBG) or photonic crystals, and electron waves in atomic crystals has motivated scientists to explore new possibilities in this field [1–5]. On account of the periodic modulations in dielectric constant in PBG crystals, with spatial periods designed to be on the order of a desired wavelength, electromagnetic waves incident along a particular direction are diffracted for a certain range of frequencies, forming stop bands. When these stop bands are wide enough and overlap for both polarization states along all crystal directions, the material possesses a complete PBG. In such a crystal, propagation of electromagnetic waves within a certain frequency range is forbidden irrespective of their direction of propagation. This leads to interesting effects in quantum optics; for example, spontaneous emission of light can be controlled, where an excited atom embedded in a PBG crystal will not be able to make a transition to a lower energy state as readily if the frequency of the emitted photon lies within the band gap, hence increasing the lifetime of the excited state [1].

Although PBG crystals will have novel applications in the optical regime, such as lowering thresholds in maintaining population inversions leading to very efficient solid state devices [1], the technological challenge of fabricating a 3D PBG crystal exhibiting a complete band gap in the optical regime has not yet been surmounted. Structures exhibiting full photonic band gaps in the microwave [6,7], millimeter [8], and submillimeter [9] regimes have already been fabricated, and a submicron length-scale photonic crystal has been proposed [10], but experimentally realizing these structures in the optical regime has remained a challenge. To carry out photonic band structure studies in the optical regime, polystyrene colloidal crystals with lattice spacings comparable to the wavelength of light have been used for this study [11,12]. These colloidal crystals consist of charged monodisperse polystyrene microspheres suspended in water, yielding a relative index of refraction of 1.20, which organize into face-centered-cubic (fcc) lattices under suitable conditions. Although such a crystal is not expected to exhibit large gaps because of the relatively low index contrast, it does permit study of photonic band structure, as reported here. The lattice parameter of these self-organizing structures can be easily tailored, providing flexibility in designing photonic crystals for use in specific spectral regions.

Illumination of a single colloidal crystal by a monochromatic laser beam can exhibit an interesting phenomenon: various dark rings and arcs (conic cross sections) superimposed on a diffusely lit background form in both transmission and reflection geometries. These patterns are called Kossel lines [11–15] and are formed by attenuated bands of diffuse light which satisfy the Bragg condition along specific angular cones, as depicted in the inset of Fig. 1. Diffuse light originates by scattering from the impurities in thick crystals such as deviations in the polystyrene sphere diameter, dislocations, and vacancies in the lattice; for thin or dilute samples, a diverging source of light can be generated with an external diffuser [11].

Figure 1 depicts simulated Kossel lines [16] for an fcc crystal with a lattice parameter of 486 nm. In each case, the incident laser beam passes through the center of each frame; each circle or arc represents a band of attenuation arising from Bragg diffraction from a specific set of planes. Bragg diffraction of the direct beam occurs at the *L* point for 752 nm light and the *X* point at 650 nm, where *L* and *X* are the symmetry points on the first Brillouin zone (FBZ) corresponding to [111] and [002] directions in the fcc crystal. The Bragg condition is satisfied by (111) and (002) planes, respectively, for these wavelengths, thus the beam is diffracted backwards and a circular dark spot appears in transmission at the center of each frame. For the transmission experiments discussed below (see Fig. 3), such Bragg diffraction of the direct beam leads to a strong attenuation feature in the spectrum. Simultaneous satisfaction of the Bragg condition by two sets of crystal planes can be observed where two circles touch at the center of the frame (e.g., at *K* and *U* points at 614 nm). In Fig. 2, the Kossel line pattern for 583 nm about the *W* point formed by the intersection of three circles is shown along with the fcc symmetry points.

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Kossel lines are useful for establishing single crystallinity and lattice type, and are essential for orienting crystals where the symmetry directions are not known *a priori*. Even for structures fabricated with known symmetry directions, exact orientation may be possible *only* by inspection of Kossel lines, since the index of refraction of a photonic crystal along a particular direction is not well known owing to the anomalous index of refraction at the band edges [17,18]. For a crystal with a complete PBG, where no light is transmitted, the Kossel lines formed in reflection can still be used for exact alignment.

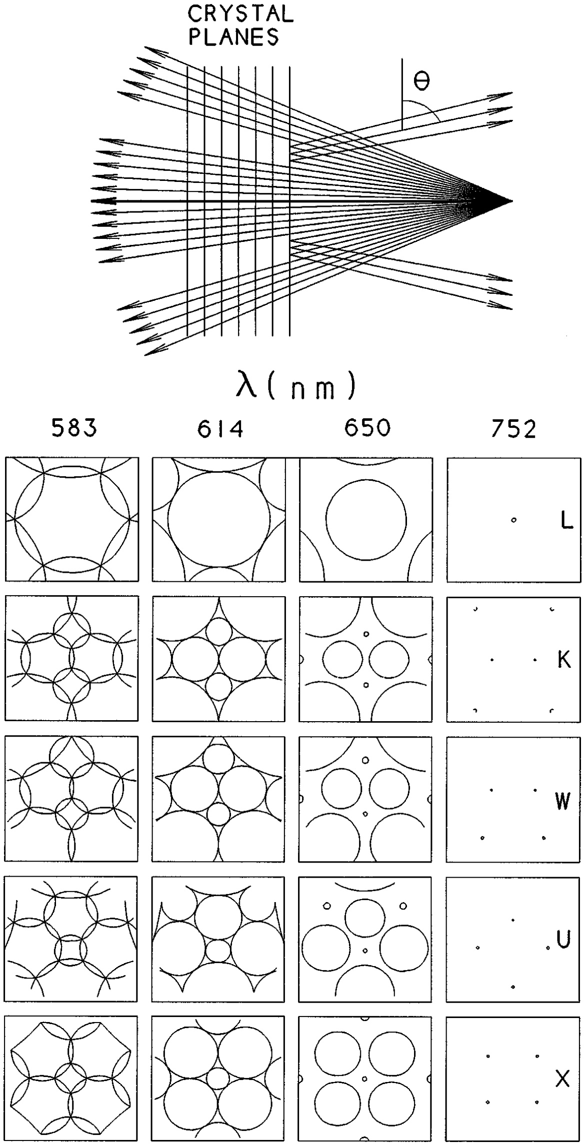

FIG. 1. Simulated Kossel line patterns for an fcc crystal, with a lattice parameter of 486 nm, along several symmetry directions. Each row shows patterns obtained along the same direction for different wavelengths. Each frame represents a 180° field of view, except for the first row, which is 90°. Inset: Formation of Kossel lines. Parallel lines represent crystal planes in a photonic crystal and the probe beam is incident perpendicular to these planes. Some light is diffused and propagates through the crystal in all directions, as indicated by the arrows. For a given wavelength, light traveling only along a certain direction (in this case with an angle about θ from the crystal planes) can satisfy the Bragg condition. Such Bragg diffraction leads to a conical band of attenuation that forms the Kossel line pattern on intersection with a screen, as depicted in Fig. 2.

By varying the crystal orientation and illumination wavelength, Kossel line patterns can also provide a visual mapping of the photonic band structure. A complete PBG would be signified by the presence of Kossel lines along each direction for a given wavelength (center of each frame along a column of the matrix in Fig. 1). For example, at 583 nm this is only satisfied by the *W* point; the Kossel pattern about the *L* point indicates the absence of a band gap at this wavelength. Thus the fcc lattice does not produce readily overlapping stop bands. A complete PBG is indicated when the widths of the Kossel line patterns are sufficient to generate overlap for all orientations.

To measure photonic band structure in the visible regime, a 5.0% volume fraction colloidal crystal was prepared with 0.135 μm mean diameter polystyrene microspheres, monodisperse to within 4.2% [19]. The microspheres have a permanent net negative surface charge

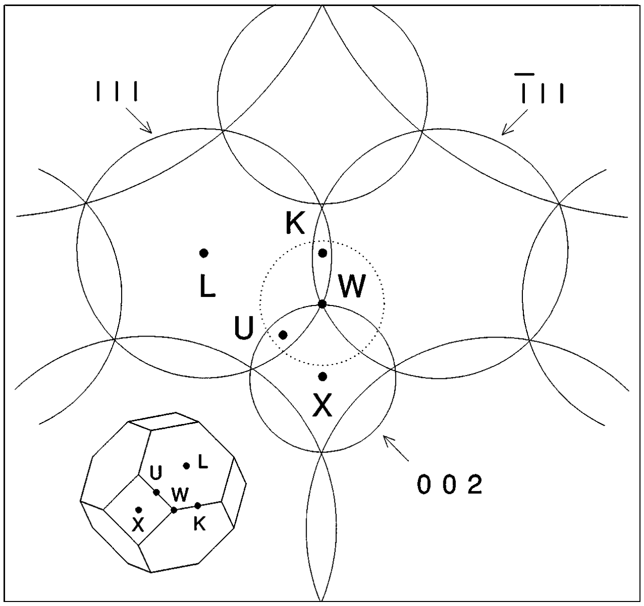

FIG. 2. Simulated Kossel line pattern (projected on a hemispherical surface) obtained along the [012] direction, corresponding to the *W* point, for $\lambda = 583$ nm. In our experiment, the wavelength of the dye laser is adjusted so that the intersection of the 111, 111, and 002 Kossel lines are obtained. Initially the crystal was oriented so that the incoming beam was along the [111] direction (*L* point). Then the crystal was rotated from the *L* point to the *W* point until the center of the intersection region of the three Kossel lines blocked the transmitted beam. The area inside the broken circle indicates our experimentally observable area at this orientation. The symmetry points of the first Brillouin zone for the fcc crystal are identified in the inset.

counterbalanced by positively charged counterions. Stray ions are also present in the suspension, decreasing the Debye screening length. Once the stray ions are removed with ion-exchange resin, the microspheres interact with a short range repulsive Coulomb force, in addition to a long range attractive van der Waals force [12]. The colloidal suspension subsequently undergoes a phase transition from a disordered state to an fcc lattice (for this volume fraction and microsphere diameter). The thickness of the crystal studied here was around 450 μm, which resulted in about ~1700 layers of (111) planes.

fcc colloidal crystals grow with the densest planes (111) parallel to the sample cell windows. Since the only crystal direction known *a priori* is the [111] direction (*L* point), the remaining orientational information was obtained via Kossel line analysis. The major criterion in the adjustment of the lattice spacing of the sample was to obtain *K*, *U*, and *W* points (see Fig. 2) on the fcc FBZ (i.e., corresponding Kossel lines) within the wavelength range of the dye laser (R6G ~ 575–625 nm). After aligning the crystals, a UV–visible–near-infrared spectrophotometer was used to obtain transmission spectra over a much wider range than possible with the dye laser used for observing Kossel line. Transmission spectra were obtained for both orthogonal components of the plane-polarized beam along directions between the *L* and *W* points. The transmitted beam and diffuse light were collected with a large aperture lens and focused on an optical detector.

In Fig. 3 transmission measurements show optical stop bands opening up at least 2 orders of magnitude deep. The dramatic variation of the stop bands as a function of crystal angle is evident. In moving from the *L* point to the *W* point, the center of the stop band shifts by ~130 nm. This shift is not surprising since the *L* point is closest to the center of the FBZ while the *W* point is the furthest from the center. If the FBZ of the lattice were more spherical than that of the fcc crystal, the frequency shift would be smaller. A convergence of two bands at the *W* point is evident, and the stop band at the *W* point (0.145 eV) is much wider than at the *L* point (0.021 eV), an unexpected result [20]. The bandwidths of the gaps are presented in Fig. 4, extracted from the full widths $\Delta\lambda$ of the normalized transmission bands in Fig. 3 at 2 orders of magnitude below unity transmission. Furthermore, on examination of the different polarization states in the crystal [21], the degeneracy expected at the *W* point for a spherically symmetric basis (as with microspheres) [20] is not found for reasons yet uncertain. Additional theoretical work on photonic band structure of fcc polystyrene colloidal crystals would be helpful in elucidating the reasons for these discrepancies.

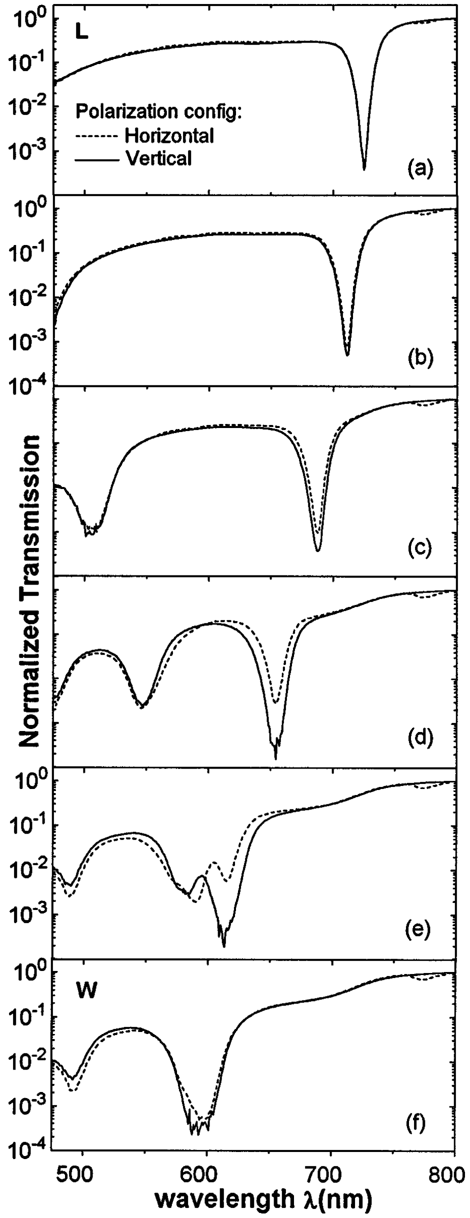

FIG. 3. Normalized transmission spectra taken along the *L*-*W* directions for an fcc lattice formed by ordered 0.135 μm diameter polystyrene microspheres with a lattice constant of 469 nm. Dashed (solid) lines are guides to the eye indicating horizontally (vertically) polarized incoming probe beam. (a) *L* point, (b) *L* + 16°, (c) *L* + 26°, (d) *L* + 36°, (e) *L* + 47°, and (f) *W* point (*L* + 51.1°).

In Fig. 3(a) the decline in transmission around 500 nm arises possibly from increased scattering cross section at shorter wavelengths mainly due to residual disorder caused by the impurities, increased absorption of polystyrene, and a second-order Bragg minimum which is expected around 400 nm. The minimum of the second-order gap is expected to be located at one-half of the first-order gap minimum but may be shifted owing to anomalous dispersion.

In summary, observation of Kossel line patterns from these structures opens up the possibility of another tool for the investigation of PBG crystals, providing a visual representation of the photonic band structure of the underlying lattice. Moreover, given a new candidate (lattice) for a PBG structure, its Kossel line patterns can provide a quick check for overlapping stop bands. Most importantly,

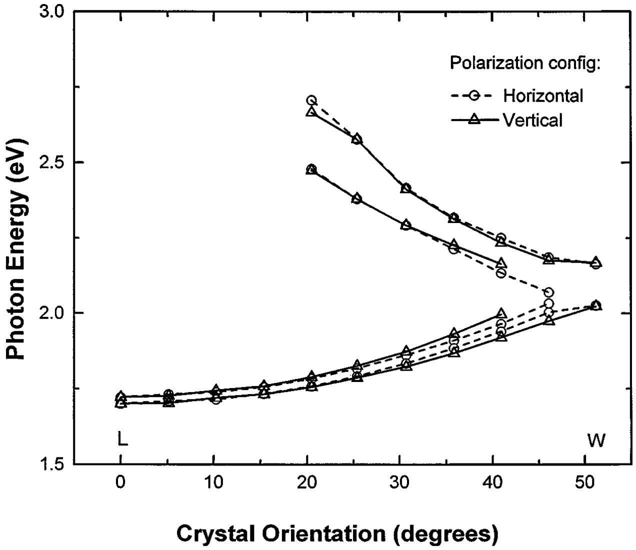

FIG. 4. Photonic band structure, obtained from the transmission spectra in Fig. 3, for an fcc crystal of 0.135 μm diameter polystyrene microspheres with a lattice constant of 469 nm.

Kossel lines also provide an exact experimental method for locating the symmetry directions of a single crystalline sample. In this study, the symmetry directions of a 3D photonic crystal have been experimentally obtained with Kossel line analysis, and the transmission measurements along these directions show optical stop bands opening up at least 2 orders of magnitude deep. As expected the photonic band structure did not yield a complete gap along the L-W points; however, the expected degeneracy at the W point was not observed.

Experimental investigation of the impurity modes for this system might also be a possibility with a slightly disordered sample. An intriguing possibility is substitutional doping of some of the polystyrene microspheres with scatterers of the same size but having different dielectric strength, thereby preserving the crystalline order but introducing optical disorder. Finally, colloidal crystals provide flexibility in designing photonic crystals with lattice parameters tailored for use in specific spectral regions.

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