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Photonic band gaps of porous solids

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Colloidal inverse photonic crystals composed of ordered lattices of air spheres in a high dielectric background are found to have three-dimensional photonic gaps for face-centered cubic, hexgaonal close-packed, and double hexagonal close-packed stacking sequences. Conditions for the occurrence of the complete gap are a sufficient dielectric contrast and a geometry near close packed. Although the lower pseudogaps of these stacking sequences differ, the lowest stop band in the stacking direction is insensitive to the stacking sequence; hence their experimental reflection should be similar. Transmission calculations with structural disorder show the lower pseudogap is relatively unaffected but the higher gap is very difficult to observe with moderate disorder.

I. INTRODUCTION

Photonic band-gap (PBG) materials have emerged as new class of engineered structures where electromagnetic wave propagation is forbidden in a certain frequency region—the photonic band gap.[1–4] A major thrust has been to design and fabricate photonic crystals at optical length scales. PBG crystals at optical wavelengths offer new ways to manipulate light and have several potential applications to higher efficiency lasers, optical communications, and in catalysis.

We focus here on three-dimensional (3D) photonic crystals, where the propagation of waves is forbidden for all directions at frequencies within the band gap. Microelectronic fabrication techniques for 3D crystals at optical length scales are very difficult, although much progress has recently been made in fabricating 3D-PBG crystals at near-infrared wavelengths.[5,6] Since three-dimensional colloidal crystals self-assemble with excellent long-range periodicity at optical length scales, these colloidal crystals have emerged as very promising candidates for photonic band-gap structures. Recently several groups have fabricated colloidal crystals at optical length scales[7–12] and have studied photonic effects.

Theoretical studies have identified the ''inverse'' face-centered cubic (fcc) structure as one of the best suited for photonic band gaps. This consists of a periodic array of close-packed low dielectric spheres with refractive index n_1 in a high dielectric background with refractive index n_2, generating the refractive index contrast $n=n_2/n_1$. The spheres may be air ($n_1=1$) enclosed by the interconnected higher dielectric background. Calculations have found the inverse fcc structure to have both a low-frequency pseudogap and a high frequency three-dimensional band gap.[13–17] The inverse structure has much more desirable photonic gaps than the direct structure of close-packed dielectric spheres,[15] which has been synthesized earlier by several groups.[18–25]

This inverse close-packed structure has been synthesized by several groups[7–12] by first crystallizing a close-packed array of polystyrene or silica spheres from a monodisperse suspension. The interstitial regions of this template were then infiltrated with titania or other polymer material through a sol-gel process. We have also achieved this structure by a somewhat different ceramic technique where the ordering and filling process was performed simultaneously.[9] The spheres were then removed by calcination or etching, leaving a macroporous solid where close-packed spherical air cavities are enclosed by a high dielectric matrix.[7–12]

However, experimental crystallization of close packed colloids generates packing sequences that differ from fcc structures and may even be random. Recent fabrication of close-packed colloids have their growth direction along the dense 111 hexagonal planes. The 111 planes suffer from twinning, i.e., the next layer can occupy two equivalent positions. The structure may not be pure fcc or hcp. An experimental solution is to use a fcc 100 template, since the 100 plane does not permit twinning, and very high-quality single crystals have been synthesized by colloidal epitaxy.[21]

Although the fcc structure is speculated to have the lowest free energy, the free energy differences from other close-packed stacking sequences is very small. We have indeed observed[9] different stacking sequences is scanning electron microscope images of close-packed air spheres in a titania matrix. Hence we investigate in this paper the dependence of the photonic properties on (i) the stacking sequence and (ii) on the structural disorder that invariably occurs during the synthesis. These calculations provide important limits for experimental observation of photonic gaps in colloidal crystals.

II. COMPUTATIONAL METHOD

The calculations are based on the well-established plane-wave expansion technique.[26–30,4,31] Here vector-wave solutions of Maxwell's equations in a periodic dielectric structure are found from a plane-wave expansion of the **E** and **H** fields. The spatially periodic dielectric function $\epsilon(r)$ is expanded in plane waves to yield $\epsilon(G)$. The dielectric matrix in Fourier space is then inverted to yield $\epsilon^{-1}(G-G')$, which is used in the calculations. Matrix diagonalization yields the band frequencies $\omega(k)$ for each wave vector k.

III. RESULTS

The inverse fcc structure is known to have a full gap between the 8 and 9 bands,[13–17] which has its largest magnitude near the close-packed geometry (filling fraction $f = 0.74$). For all filling ratios the dielectric background forms a multiply connected network. A minimum refractive index contrast $n_1/n_2 > 2.9$ is needed to obtain this full gap, although the lower frequency pseudogap is observable at much lower contrasts. For spherical air cavities in silicon ($n = 3.4$) or GaAs ($n = 3.6$), both the pseudogap and full gap should be observable, whereas for titania as background ($n = 2.5$–2.7) only the pseudogap exists. For spherical air cavities of diameter 290 nm in a background $n = 3.1$, we expect the pseudogap at 719 nm and the full gap at 473 nm.

Microelectronic methods are difficult[32,33] but were used to fabricate an fcc crystal by stacking dielectric slabs containing a triangular lattice of air cylinders.[34] However the cylinders break the spherical symmetry of the lattice, and lead to a closure of the full gap since the cubic symmetry is lost. The lowest frequency stop band is still observed.[34]

Colloidal systems using titania or similar ceramic material as the background suffer from having a low dielectric contrast. Although titania has a refractive index (n) between 2.5 and 2.7 at optical wavelengths, a lower density of titania may result from ceramic processing or sol-gel methods, resulting in a substantially lower refractive index ($n \approx 2$). We ask what would the experimental signature of such inverse fcc or similar structures be for such realistic dielectric contrasts? Optical measurements[7,9] of the transmission or reflection reveal stop bands along the 111 stacking direction of the crystal. We calculate the stop bands along the 111 direction (Fig. 1) for a lower but realistic contrast of $n = 2$. There are a rich variety of stop bands as a function of the filling ratio. The lowest stop band is very wide, corresponding to the pseudogap region, and would generate a strong reflection peak, or a transmission dip for sufficiently thin films, at a wavelength close to twice the sphere diameter (for $f \sim 0.7$).

At shorter wavelengths, there are two closely spaced stop bands for filling ratios above 0.6 (Fig. 1). Of these, the shorter wavelength stop band is the remnant of the full 8–9 gap. At lower filling ratios ($f \leqslant 0.6$) these stop bands disappear but a new narrow stop band (between bands 10 and 11) appears. As filling ratios are decreased below 0.7, another stop band (between bands 16 and 17) opens up and persists down to low filling ratios. Even though the dielectric contrast is not sufficient to open a full gap, the reflection from the close-packed 111 layers should contain a strong peak from the lowest stopband or pseudogap. There should be additional multiple-reflection peaks from these higher stop bands, whose positions are dependent on filling ratios.

High-contrast fcc lattices have a spectrum of stop bands in the 111 and 100 directions.[16,31,35] However for lower contrast (e.g. $n = 2$), only the stopbands in the 111 direction remain, and no stopbands are found in the 100 direction, due to band overlap. For low contrasts, it is experimentally advantageous to fabricate the lattice stacked along the close-packed direction, to observe stopbands.

Experimentally, colloidal crystals may stack in a hexagonal close-packed (hcp) structure with the stacking sequence ABAB, rather than the fcc structure. The hcp structure also has a remarkable full gap at higher frequency between the 16 and 17 bands, very similar to that of the fcc structure.[16] This full gap opens up for refractive index contrast $n_1/n_2 > 3.1$. The minimum refractive index contrast needed to observe this gap ($\simeq 3.1$, Fig. 2) is larger than that found for the fcc structure ($\simeq 2.9$). The size of the gap for the hcp structure is optimized for a larger air filling ratio of air, close to $f \simeq 0.8$, resulting in a more sparse structure, rather than the close-packed geometry. Spontaneous emission may be inhibited and lifetimes of excited states increased, for emission frequencies within the full band gap of these structures.

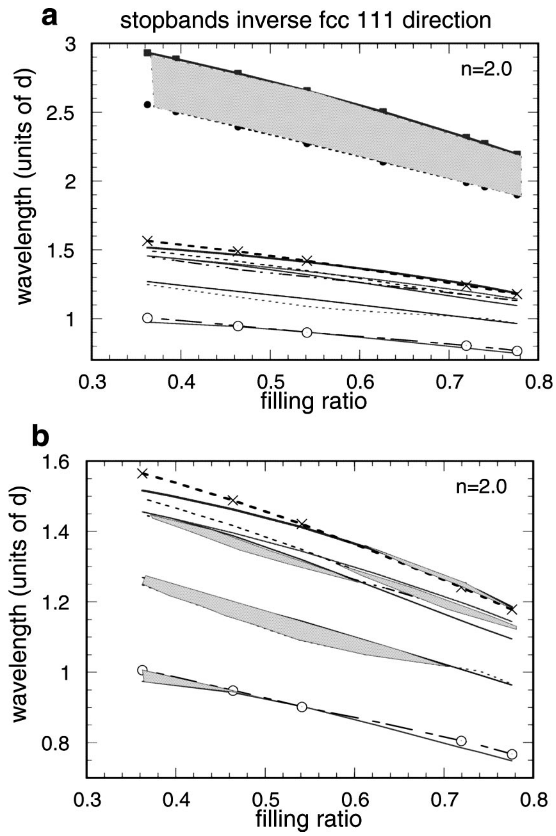

FIG. 1. (a) The photonic stop bands for propagation along the 111 stacking direction of the inverse fcc lattice as a function of the filling ratio. Stop band wavelengths are in units of d, the center-to-center separation between the spheres. A realistic refractive index ($n = 2$) is used. Bands are displayed by lines. Band gaps are the shaded regions. The longest wavelength stop band corresponds to the pseudogap region and is shaded. (b) The higher bands are enlarged and shaded regions display the stop bands.

We compare the experimental signature of reflection and transmission from the hcp stacking with the fcc stacking, by calculating the stop bands of the hcp structure along the 001 stacking direction. As in the fcc calculation we use a realistic but lower refractive index contrast of 2. The stop bands in the stacking direction show (Fig. 3) a wide stop band (between bands 4 and 5) at the same wavelength as in the fcc structure. This stop band is independent of the stacking sequence.

There are further narrow stop bands in the hcp structure at shorter wavelengths (Fig. 3) that are somewhat different from the fcc case. Unlike the fcc case, we do not find a wide

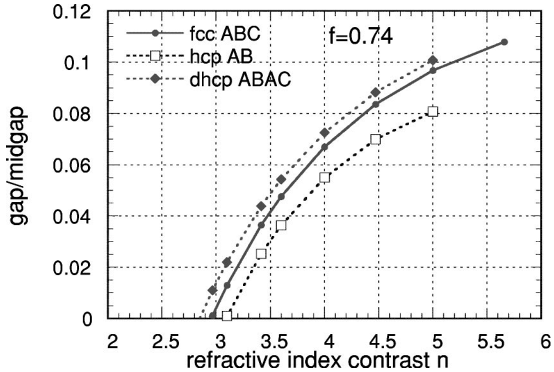

FIG. 2. The magnitude of the 3D band gap as a function of the refractive index for the hcp, dhcp, and fcc stacking sequences of air spheres. All the calculations are for a filling ratio of 0.74 corresponding to touching spheres.

higher-frequency stop band opening up for filling ratios below 0.7. In addition, there are band touching degeneracies that may generate significant reflection signatures. Most importantly, photonic crystals with both stacking sequences should have a strong reflectivity peak corresponding to the first stop band, which depends only on the local order.

In experiments a uniaxial compression of the structure may occur from the pressing of the nanostructured titania film with air pores during synthesis.[9] Our calculations find that the width of the lowest stop band decreases and the higher stop bands become less significant, with uniaxial compression.

A viable alternative to the hcp and fcc structures is the double hexagonal close-packed (dhcp) structure with the stacking sequence *ABAC* i.e., a repeat sequence of four layers. The dhcp structure is found in the crystal structures of the rare-earth metals Am, La, Nd, and Pr.[36] The free energy of a dhcp colloidal crystal should be very similar to the hcp colloidal crystal.

The calculated density of states (DOS) for the ''inverse'' dhcp structure (Fig. 4) shows a similar higher band gap at

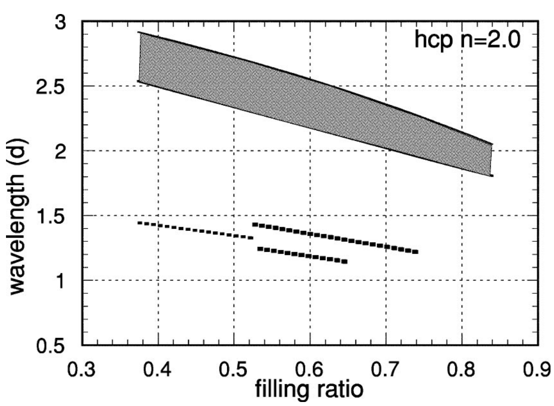

FIG. 3. The photonic stop bands for propagation along the 001 stacking direction of the inverse hcp lattice as a function of the filling ratio. Stop band wavelengths are in units of *d*, the center-to-center separation between the spheres. A realistic refractive index ($n=2$) is used. The wide, longest wavelength stop band (shaded region) corresponds to the pseudogap region. For clarity individual bands are not shown. Dashed lines indicate the narrow stop bands at shorter wavelengths.

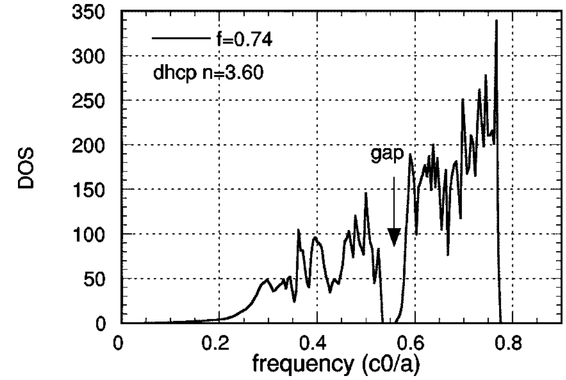

FIG. 4. Photonic densities of states for the dhcp structure (with stacking sequence ABAC), at the close-packed geometry of touching air spheres ($f=0.74$). A refractive index contrast of 3.6 is used.

virtually the same frequency as in the hcp structure. The minimum refractive index contrast needed for this gap is $\simeq 2.8$, substantially lower than that in the hcp structure, and slightly lower than that for the fcc structure (Fig. 2). Hence the dhcp stacking has advantages over the hcp structure. The full gap is also larger for the dhcp stacking than for the hcp structure at the close-packed geometry ($f=0.74$). Although there is no low-frequency pseudogap in either the dhcp or hcp structures the lowest stop band is very similar for both stacking sequences, and similar to the results in Fig. 3.

It is interesting to compare the photonic properties of the high-symmetry body-centered-cubic (bcc) structure to these close-packed geometries, since bcc colloidal crystals can be synthesized.[20] The bcc lattice of air spheres in a background dielectric of $n=3.6$ has a high-frequency pseudogap (Fig. 5) for the porous structure with a high packing fraction of air ($f=0.8$), corresponding to overlapping air cavities. In terms of the sphere radii (R), the bcc pseudogap frequency occurs at $0.28c_0/R$ compared to $0.27c_0/R$ for the fcc full gap, for the contrast $n=3.60$. Occurrence of the higher gap is a common feature in high-symmetry inverse crystal lattices. This bcc pseudogap does not appear for lower dielectric contrasts such as $n=3.1$. The bcc lattice composed of a cylindrical elements has been found earlier to have a full band gap.[37]

IV. DISORDER AND PHOTONIC GAPS

Experimentally fabricated colloidal crystals have a considerable degree of disorder, and can display[9] point defects

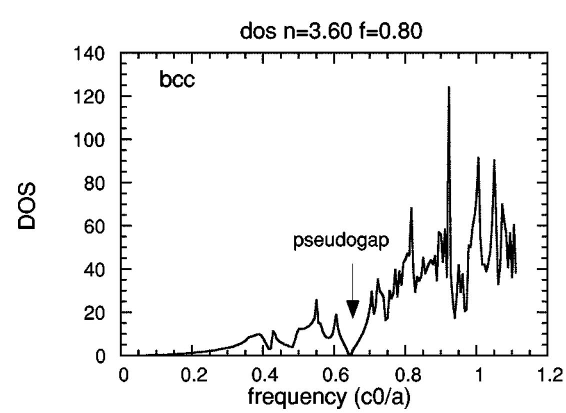

FIG. 5. Photonic densities of states for the body-centered-cubic (bcc) lattice of air spheres for a filling ratio of 0.8, corresponding to overlapping air spheres. The refractive index contrast of 3.6 is used.

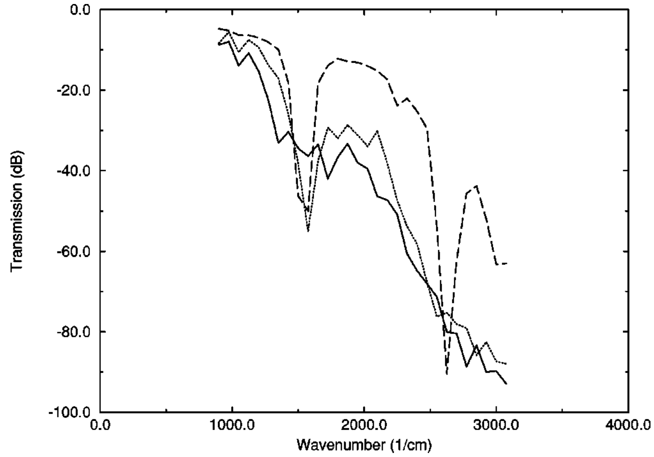

FIG. 6. Transmission through a fcc lattice of air spheres as a function of the frequency, calculated with the transfer matrix method. Dashed line is the case of the ideal crystal showing both the lower pseudogap and the higher full gap. Dotted and solid lines are for disorder in the positions of the spheres where the mean positions of the spheres are displaced by an amount d/a of 0.1 and 0.2, respectively. A large system of 12 unit cells (36 layers) was used in the stacking direction. A filling ratio of 0.6 and refractive index contrast of 2.23 was used. A realistic but small absorption ($\mathrm{Im}\epsilon = 0.1$) was also used.

in the form of vacancies and domains where the orientation of the triangular lattice differs across the domain boundary. It is then important to evaluate the sensitivity of the photonic gaps to disorder. We considered the fcc structure of air spheres in a low dielectric background of $n = 2.23$ ($\epsilon = 5$) to account for experimental porosity of the background ceramic. A filling fraction of 0.6 was used consistent with an estimation of the packing in the experimental structure. A realistic absorption $[\mathrm{Im}(\epsilon) = 0.1]$ was included in the transfer matrix calculations. A supercell was used perpendicular to the stacking direction. For the ideal crystal, the calculated transmission shows pronounced dips at both the pseudogap and full gap frequencies (Fig. 6). Disorder is then introduced in the positions of the air spheres that can randomly vary by an amount d along each direction. For a 10% disorder in d/a (a is the lattice constant) the pseudogap is still observed, but the higher gap can no longer be observed in transmission, which just decreases at higher frequencies (Fig. 6). For higher disorder in sphere positions of 20% the pseudogap is also very weak (Fig. 6) and appears as just a shoulder in the transmission.

These results suggest that the full 3D higher gap is very sensitive to disorder and cannot be observed for moderate amounts of disorder. In contrast the lower pseudogap is relatively robust to disorder. In the inverse fcc structure with a moderate amount of disorder, we expect the lowest stop band should still be observed. This is physically reasonable since the phase of the electromagnetic wave oscillates rapidly in the unit cell for higher frequencies or large wave vector k, and can be more strongly affected by variation of the positions of the scattering centers in the unit cell. We extend this analysis to the hcp and dhcp structures and conclude that with high disorder the full gap will no longer be observable in either of these structures.

Similar sensitivities of gaps to absorption have been

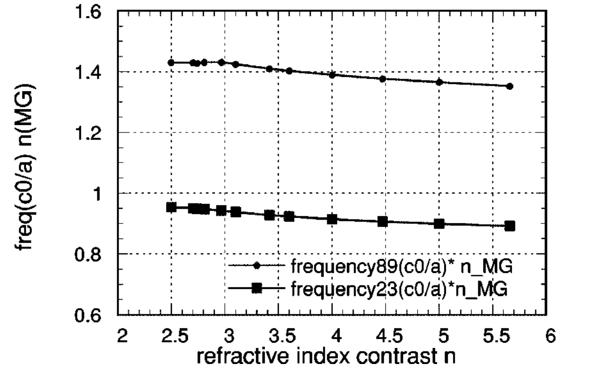

FIG. 7. The product of the midgap frequencies and the Maxwell-Garnett effective refractive index, as a function of the background refractive index n. Calculations are for touching air spheres ($f = 0.74$).

found earlier,[15] where the lower frequency pseudogap was relatively unaffected by moderate absorption, whereas the higher gap was no longer observable.

Another possibility is when the structure is very well ordered within the close-packed planes, and the only disorder is in the stacking sequence of the planes, resulting in a random packing sequence. In this case, we expect the structure to still show a higher gap, but states may be introduced inside the gap.

V. EFFECTIVE-MEDIUM APPROXIMATION

In the effective-medium approximation[38] the scalar wave effective dielectric constant is a poor representation of the effective dielectric constant as inferred from the long-wavelength limit of the modes. Instead the Maxwell-Garnett effective dielectric constant was found to very well represent the long-wavelength limit of various photonic lattices, including the fcc lattice.[38] Here the Maxwell-Garnett effective dielectric constant is

$$\epsilon_{MG} = \epsilon_1[\epsilon_1 + 1 + 2f(1-\epsilon_1)]/[2\epsilon_1 + 1 - f(1-\epsilon_1)]. \quad (1)$$

Here f is the filling fraction of air and ϵ_1 the dielectric constant of the background medium.

From effective-medium theories the product of the midgap frequency and the Maxwell-Garnett refractive index contrast is expected to be a constant. We plot this product (Fig. 7) and indeed find the product νn_{MG} to be almost independent of n, confirming that the Maxwell-Garnett effective-medium approximation works very well.

VI. SUMMARY

In summary we have calculated the photonic band structure of the inverse fcc, hcp, and dhcp structures. The dhcp structure shows a full higher frequency band gap similar to that found for the fcc and hcp structures. For a low dielectric contrast where the full band gap is no longer present, all of these structures exhibit a wide stop band in the 111 direction, observable as a strong peak in reflection from the close-packed planes. The full band gap is very sensitive to disorder and absorption, and cannot be observed with moderate disorder.

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