

Polarization dependence of crystalline colloidal array diffraction

Guisheng Pan, Ajay K. Sood,^{a)} and Sanford A. Asher^{b)}

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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We measured the polarization dependence of the Bragg diffraction efficiency of a crystalline colloidal array and compared the experimental results to that predicted by theory. The diffraction efficiency for π polarized light decreases to zero for an incidence angle of 45° to the diffracting planes. Our experimental diffraction and transmission results quantitatively agree with the predictions of dynamical diffraction theory. © 1998 American Institute of Physics.

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I. INTRODUCTION

Crystalline colloidal arrays (CCAs) form spontaneously through the self assembly of monodisperse charged colloidal spheres in low ionic strength aqueous solutions.¹⁻⁶ The Coulombic repulsive interactions between charged submicrometer colloidal spheres result in the formation of either body centered cubic (bcc) or face centered cubic (fcc) arrays of colloidal particles.^{3,5} These CCAs can efficiently Bragg diffract light in the ultraviolet, visible and near infrared spectral regions, depending on their lattice spacings.^{7,8} These properties of CCA have been utilized to make devices such as narrow band optical rejection filters,^{4,7,9-11} optically nonlinear limiters and switching devices,¹²⁻¹⁶ and chemical sensing devices.¹⁷

The diffraction from these CCAs occurs in the dynamical diffraction limit^{6,10,18} and a few studies have modeled the efficiencies and bandwidths of the diffracted and transmitted light.^{6,19,20} Recently a number of studies has experimentally examined diffraction and transmission from CCAs and a polarization dependence for the transmitted light has been observed. For example, Jethmalani *et al.*²¹ used polarized optical microscopy to study the nucleation, growth and morphology of a CCA of silica spheres polymerized in poly(methyl methacrylate) and noted that the crystals were birefringent. Monovoukas *et al.*^{22,23} studied the optical anisotropy of polystyrene CCA crystallites more exhaustively by measuring the transmitted light intensity and the dichroism of the transmitted light as a function of crystallite orientation and incident light polarization. They concluded that the dichroism observed was consistent with predictions of dynamical diffraction theory,^{6,10,18} which predicts a large dependence of the diffraction efficiency upon the incident light polarization. Our study here directly examines the polarization dependence of the diffracted light and finds good agreement with dynamical diffraction theory.

II. EXPERIMENT

We synthesized polystyrene colloidal particles with diameters of 150 nm and 14 000 surface charges per particle as measured by conductometric titrations. The CCA was prepared according to procedures reported previously.⁴ The CCA was injected between a pair of quartz windows separated by a 100 μm thick spacer. Transmission measurements were made by mounting this sample cell vertically at the center of a Pyrex glass cylinder filled with glycerol ($n_D = 1.474$), in order to refractive index match the Pyrex glass ($n_D = 1.474$), so as to minimize surface reflections. This assembly was mounted on a rotation stage and placed in a Perkin-Elmer Lambda 9 ultraviolet (UV)-visible-near infrared (IR) spectrophotometer to measure the CCA transmission spectra as a function of incidence angle. A polarizer in front of the sample polarized the incident light either in the incident plane (π) or perpendicular to it (σ).

The polarization dependence of the diffracted light was measured using the apparatus shown in Fig. 1. Incident illumination derived from a Spectra Physics model 164 argon ion laser with a broadband rear reflector was used in order to simultaneously obtain all of the lasing emission wavelengths. A polarization rotator defined the polarization angle of the incident light. The light diffracted by the CCA was focused onto a photodetector and measured by a radiometer (Laser Probe model RM-6600).

III. RESULTS AND DISCUSSION

A. Theory

Bragg diffraction by CCA can be described by dynamical diffraction theory which models the propagation of the coupled incident and diffracted beams.^{6,10,18} This theory predicts a small variation between the dynamical diffracted wavelength, λ'_B for a particular incidence angle and the wavelength predicted by the simple Bragg equation $\lambda_B = 2n_s d_{hkl} \sin(\theta_B)$, which operates in the kinematic diffraction regime.

Dynamical diffraction theory predicts^{6,10,18,23}

$$\lambda'_B = \lambda_B \left(1 - \frac{\varphi'_0}{2 \sin^2 \theta_B} \right)$$

^{a)}Permanent address: Department of Physics, India Institute of Science, Bangalore 560012, India.

^{b)}Author to whom correspondence should be addressed; electronic mail: asher+@pitt.edu

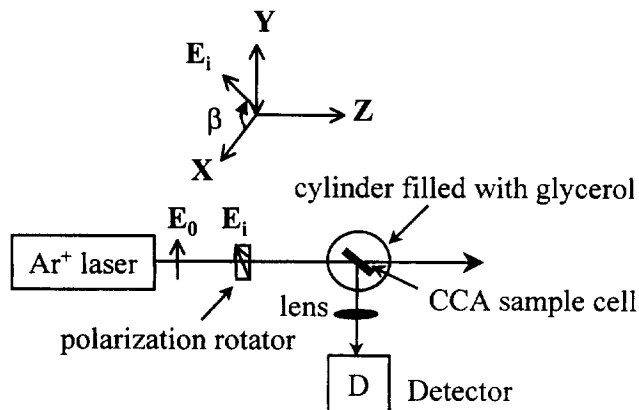


FIG. 1. Schematic of diffraction measurement. The vertically polarized laser beam with an electric field, E_0 , propagates along the Z direction. The polarization rotator adjusts the polarization angle (β) of the laser beam. The CCA sample cell was mounted vertically at the center of a Pyrex cylinder and immersed in a reservoir of glycerol. The laser beam diffracted by the CCA was focused and measured by a detector.

where (1)

$$\varphi'_0 = 3\phi \frac{(m^2 - 1)}{(m^2 + 2)},$$

where λ_B is the wavelength in air of the Bragg diffracted light. n_s is the refractive index of the CCA system. d_{hkl} is the interplanar spacing of the lattice plane with Miller indices (hkl). θ_B is the Bragg glancing angle for the beam incident on the (hkl) plane within the crystal. φ'_0 is the real part of the crystal polarizability, m is the refractive index ratio between the particles and the aqueous medium, and ϕ is the particle volume fraction.

Dynamical diffraction theory predicts that the ratio of the maximum diffracted intensity (I_d) to the incident intensity (I_0) for a perfect crystal is^{6,10,18}

$$\frac{I_D}{I_0} = (\tanh A)^2, \quad (2)$$

where A is

$$A = \frac{2}{\pi^{3/2}} \frac{K}{\lambda_B} \left(\frac{n_s}{n_0} \right) \left(\frac{3(m^2 - 1)}{m^2 + 2} \right) (\sin u - u \cos u) \left(\frac{t_0}{\sin \theta_B} \right), \quad (3)$$

where K is the polarization factor, n_0 is the refractive index of air, t_0 is the crystal thickness and u is the scattering size parameter

$$u = \frac{2\pi n D_0 \sin \theta_B}{\lambda_B}, \quad (4)$$

where D_0 is the particle diameter.

Dynamical diffraction theory predicts that $K_\sigma = 1$ and $K_\pi = |\cos 2\theta_B|$, for the σ and π polarizations with respect to the incident plane. From Eqs. (2) and (3), we can see that the diffracted intensity scales with K . For normal incidence at $\theta_B = 90^\circ$, $K_\sigma = K_\pi = 1$, and the diffraction will be polarization independent. However, a polarization dependence is predicted for $\theta_B \neq 90^\circ$ ($K_\sigma > K_\pi$); in fact no diffraction is predicted for π polarized light for $\theta_B = 45^\circ$.

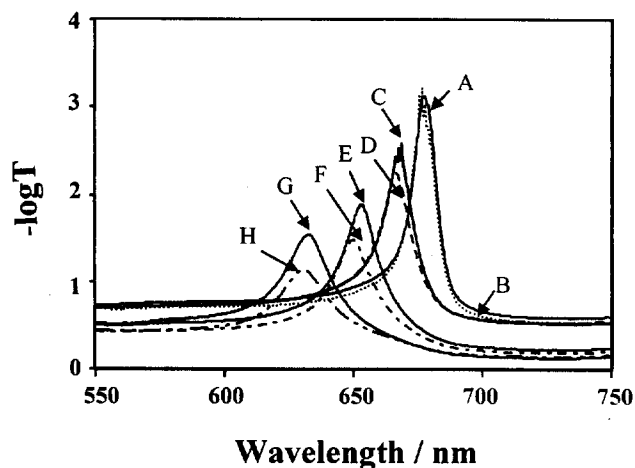


FIG. 2. Transmission spectra of a polystyrene CCA. The particle diameter is 150 nm, and the volume fraction is 12.59%. The polarization and Bragg angle (within the CCA) for curves A–F are (A) σ , 90° ; (B) π , 90° ; (C) σ , 79° ; (D) π , 79° ; (E) σ , 74° ; (F) π , 74° ; (G) σ , 68° ; (H) π , 68° . The small shifts in the diffraction wavelength result from experimental error in the angle of the sample within the spectrometer.

B. Results

Figure 2 shows the CCA transmission spectra measured at different incident angles ($\theta_i = 90^\circ, 80^\circ, 75^\circ, 70^\circ$ measured in a glycerol bath), with either σ or π incident polarization. The Bragg angle inside the CCA sample (θ_B) is calculated using Snell's law:

$$n_g \sin(90^\circ - \theta_i) = n_s \sin(90^\circ - \theta_B), \quad (5)$$

where n_g is the refractive index of glycerol. n_s is the refractive index of the CCA, which is calculated from¹⁰

$$n_s = n_w \cdot (1 - \phi_p) + n_p \cdot \phi_p, \quad (6)$$

where n_w and n_p are the refractive indices of water (1.333) and polystyrene (1.590), respectively. ϕ_p is the particle volume fraction. In our case, $\phi_p = 12.59\%$. Thus $n_s = 1.365$.

For $\theta_B = 90^\circ$, the attenuation is identical for both polarizations, in agreement with the theoretical prediction, because $K_\sigma = K_\pi = 1$. Figure 2 also demonstrates that significantly more attenuation occurs for σ than for π incident polarization for $\theta_B \neq 90^\circ$, since $K_\sigma > K_\pi$. As expected the difference between the attenuation for σ and π polarization increases as θ_B decreases ($K_\pi = |\cos 2\theta_B|$).

We can see from Eq. (3) that quantity A is proportional to K . Thus A_σ/A_π should be equal to K_σ/K_π . Quantity A can be determined from the measured extinction, $E = -\log(1 - I_d/I_0)$, through Eq. (2):

$$(1 - 10^{-E})^{1/2} = \tanh A. \quad (7)$$

Table I, which lists the calculated values of A_σ/A_π and K_σ/K_π for incidence angles of 90° to 68° , demonstrates that $A_\sigma/A_\pi \approx K_\sigma/K_\pi$ for curves A/B, C/D and E/F. For 68° , however, a small difference is evident between A_σ/A_π and K_σ/K_π . This deviation may result from diffuse scattering from defects which increases at shorter wavelengths.

We directly measured the polarization dependence of the diffracted light intensity by using a 514.5 nm incident laser beam (Fig. 1). The CCA diffracted the laser beam at an in-

TABLE I. Values of A and K at different Bragg angles, θ_B .

Curves	θ_B	A_σ	A_π	A_σ/A_π	K_σ/K_π
A/B	90	3.50	3.46	1.01	1.00
C/D	79	2.90	2.59	1.12	1.08
E/F	74	2.47	2.06	1.20	1.19
G/H	68	2.11	1.62	1.30	1.38

cence angle in the CCA of $\theta_B \approx 49^\circ$. The reflection from the sample cell surfaces, measured a few degrees from the Bragg diffraction condition, was subtracted from the total intensity measured at the Bragg angle to obtain the corrected diffracted intensity. Figure 3 shows that the diffracted intensity changes periodically with the polarization angle. For θ_B close to 45° , $K_\pi = |\cos 2\theta_B| \approx 0$. Thus the diffraction of the π polarization component for linearly polarized light, $E_i = E_0(\cos \beta, \sin \beta)$, becomes negligible. The projection of its electric field on the Y axis is the σ polarization component, $E_{\sigma} = E_0 \sin \beta$ and therefore $I_{\sigma} = I_0 \sin^2 \beta$, which should lead to $I_{d,\sigma} \propto I_0 \sin^2 \beta$ because the diffracted light intensity is proportional to the incident light intensity. The diffracted intensity indeed linearly increases as $\sin^2 \beta$ increases (Fig. 4). The correlation coefficient is greater than 0.99.

We examined the θ_B dependence of the ratio of the diffraction with σ and π polarizations. The diffracted maximum wavelength was 676.8 nm at normal incident angle (Fig. 2). θ_B was adjusted to 45° by tuning the wavelength of the Ar⁺ laser beam between 457.9 and 514.5 nm. The maximum ($I_{d,\sigma}$) and minimum ($I_{d,\pi}$) diffracted light intensities were measured as the incident light wavelength was varied. Figure 5 shows the dependence of $I_{d,\sigma}/I_{d,\pi}$ on θ_B . We can see that the ratio of $I_{d,\sigma}/I_{d,\pi}$ is at a maximum of 135:1 when $\theta_B = 46.1^\circ$, which is very close to 45° , the predicted angle. Thus, little π polarized light is diffracted at $\sim 45^\circ$.

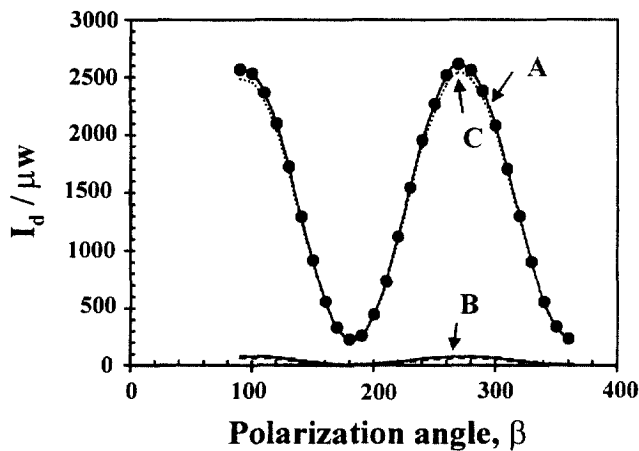


FIG. 3. Polarization dependence of diffracted intensity. The incident laser wavelength was 514.5 nm. The intensity in curve A was measured at the Bragg angle, and includes the diffracted and the incoherent scattering intensities. Curve B is the scattered intensity from the polystyrene CCA measured a few degrees ($\sim 5^\circ$) away from the Bragg angle. The corrected diffracted intensity shown in curve C was obtained by subtraction of curve B from curve A.

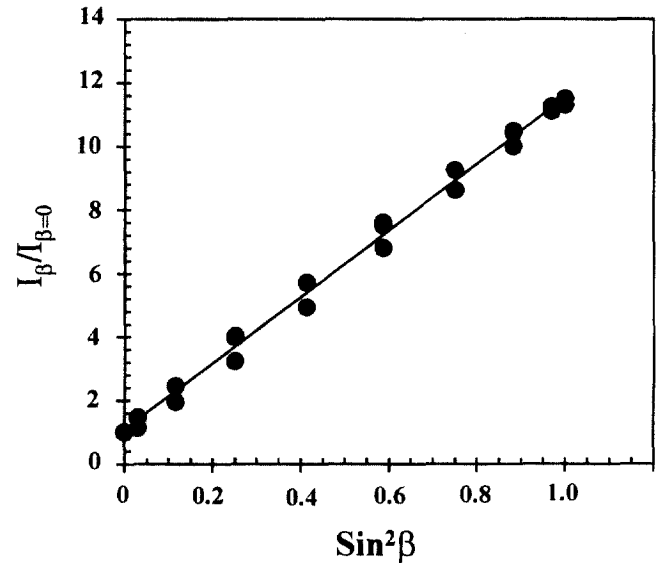


FIG. 4. Linear relationship between the diffracted intensity and $\sin^2 \beta$. I_β is the diffracted intensity measured at angle β . $I_{\beta=0}$ is the diffracted intensity when $\beta=0$. The incident laser wavelength was 514.5 nm.

III. CONCLUSIONS

Our experimental results are fully in agreement with dynamical diffraction theory that predicts that the diffraction efficiency of a crystalline colloidal array will strongly depend on the incident light polarization for light incident off the normal to the set of diffracting planes. In fact, no diffraction of the π polarization occurs for light incident at $\theta_B \approx 45^\circ$. These results indicate that the diffraction efficiency of crystalline colloidal arrays for naturally polarized light will decrease as the array is tilted off normal incidence.

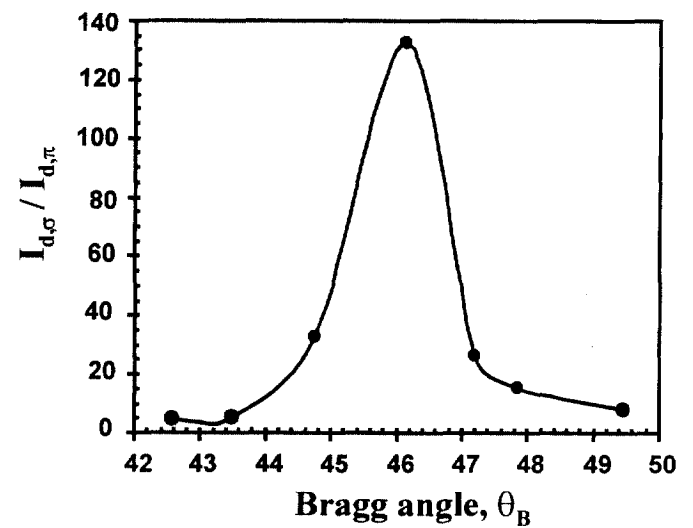


FIG. 5. Effect of the Bragg angle on the polarization dependence of the diffracted intensity. The Bragg angle was adjusted by using different laser beam wavelengths: 514.5, 501.7, 496.5, 488.0, 476.5, 465.8, and 457.9 nm. The Bragg angle was calculated by substituting the corresponding wavelength and 676.8 nm at $\theta_B = 90^\circ$ (see Fig. 2) into Eq. (1). $I_{d,\sigma}$ and $I_{d,\pi}$ are the diffracted intensities for the σ and π polarization directions. $I_{d,\sigma}/I_{d,\pi}$ is at a maximum at 488.0 nm or $\theta_B = 46.1^\circ$.

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