Chapter 1

Introduction

Many organic compounds exhibit varieties of intermediate phases in between their positionally and orientationally ordered crystalline phases and isotropic liquid phases. These intermediate phases are divided into two classes, namely, plastic crystalline phases wherein the positional order is still present but the orientational order is lost and liquid crystalline phases wherein orientational order is maintained but positional order is reduced or lost. The liquid crystalline phases have both crystal like as well as liquid like properties [1,2]. The molecules exhibiting liquid crystalline phases are geometrically anisotropic, i.e., they can be rod-like or disk-like. Phase transitions in these liquid crystalline phases can be brought about either by changing the temperature or by changing the concentration of these molecules in an appropriate solvent. The former class of materials are known as thermotropic liquid crystals and the latter are known as lyotropic liquid crystals. In this thesis we will deal only with thermotropic liquid crystals. In this chapter we briefly describe the basic classification of liquid crystals and give a brief introduction to the optical properties of the twisted liquid crystals.

1.1 Classification of thermotropic liquid crystalline phases

The thermotropic liquid crystals are classified according to the positional and orientational ordering in their molecular arrangement. Here we describe the structure of some of the liquid crystalline phases that are discussed in this thesis.

Nematic : The simplest of the liquid crystalline phases is the nematic phase. It is a fluid in which the long molecules have orientational order but no positional order in the center of masses of the various molecules. This is shown in figure 1.1a. This phase is cylindrically symmetric, i.e., optically uniaxial and centrosyrnmetric. The average orientation of the molecules can be represented by an apolar vector $\hat{\mathbf{n}}$ called director. Recently even optically biaxial nematics have been reported [3].

Cholesteric : This phase consists of non-centrosymmetric (chiral) molecules. In this phase the molecules arrange themselves in a helical structure. The phase can be described as being made up of nematic planes helically piled over one another so that the director continuously rotating uniformly about the direction normal to itself. Figure 1.1b shows the molecular arrangement in the cholesteric phase. This phase can also be obtained by doping a nematic liquid crystal with a small amount of chiral molecules. The distance P over which the director rotates by 2π is called the pitch of the medium. Since the nematic director is apolar, the cholesterics have a 2 fold screw axis. Hence the optical periodicity of the medium is $P/2$. In general this period is of the order of wavelength of light. Therefore this phase exhibits some remarkable optical properties [2,4]. Also light can be used as a probe to investigate the structure of this phase [5].

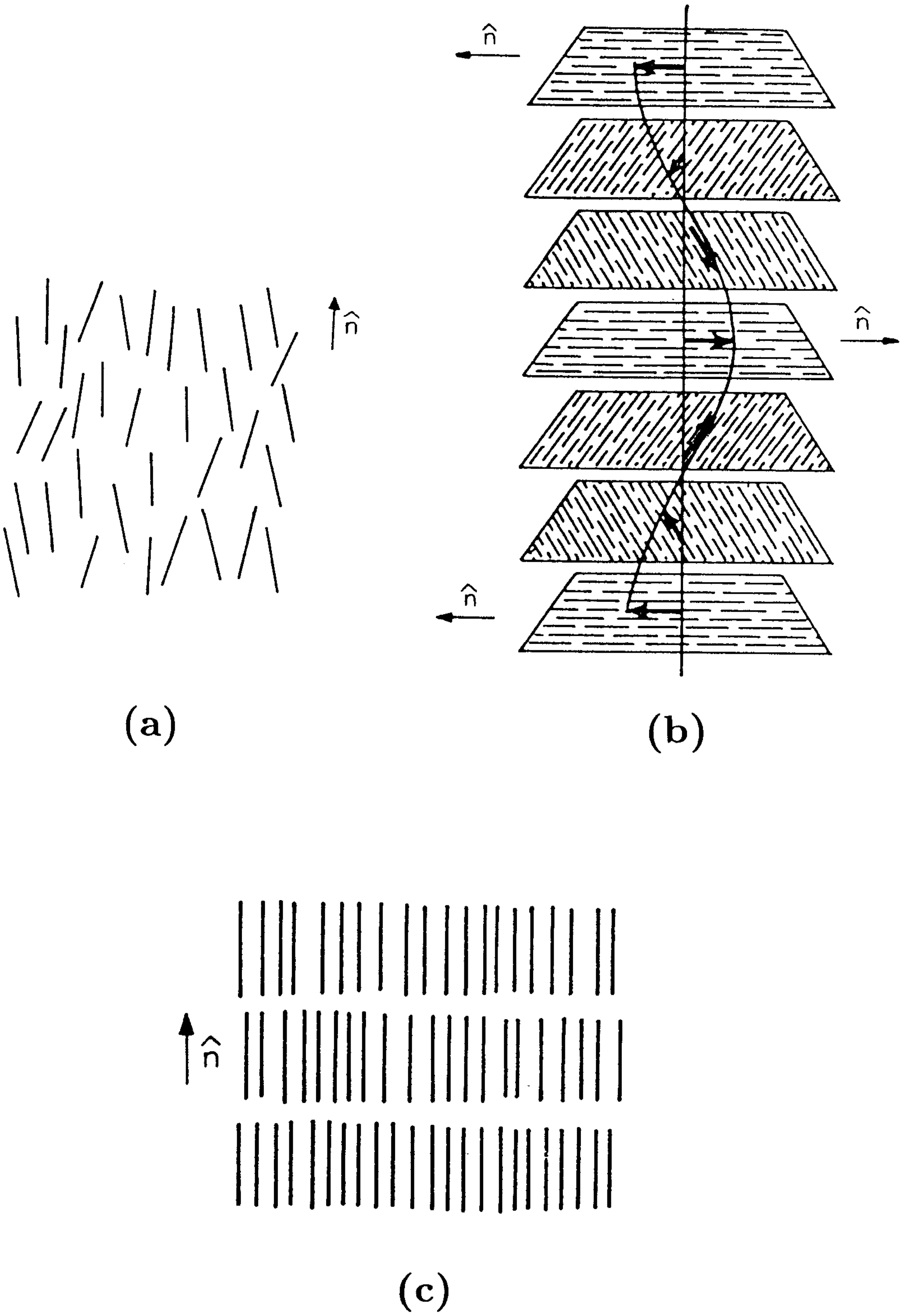

Figure 1.1: Schematic diagram of molecular arrangement in the (a) nematic, (b) cholesteric and (c) smectic A phases.

Smectic A : In this phase there is a layered arrangement of the long molecules. Within the layers the molecules have short range ordering like isotropic liquid, i.e., there is no positional order within the layers, but the average orientation of the molecules is parallel to the layer normal. This phase can be looked upon as liquid in two dimensions and crystal in the third dimension. The schematic diagram of smectic A phase is shown in figure 1.1c.

Smectic C : This phase is similar to smectic A phase except that here the molecules in the layers are tilted uniformly at an angle with respect to the layer normal. The schematic diagram of the smectic C phase is given in figure 1.2a. The projection of the molecules onto the layer plane is defined by a polar vector called the C director. If this phase is made up of chiral molecules then they form chiral smectic C phase. The molecular arrangement in chiral smectic C liquid crystal phase (Sc*) is shown in figure 1.2b. The azimuth of the tilted molecules precesses from one layer to another giving rise to a helical structure similar to the cholesteric liquid crystals, which in turn gives rise to many interesting optical properties [6,7,8]. Another consequence of the chirality of the molecules is that this phase exhibit ferroelectricity.

Ferro-liquid crystalline phases : Brochard and de Gennes [9] were first to draw attention to the physics of liquid crystals with suspended magnetic grains, also known as ferro-liquid crystals. Magnetically doped nematic, cholesteric [10,11,12], smectic [13] and lyotropic hexagonal [14] phases have indeed been made in the laboratory. In these systems the magnetization is along the local director. Schematic diagrams of magnetically doped nematic and cholesteric phases are shown in figure 1.3a and 1.3b. The arrows in the figure indicate the direction of magnetization

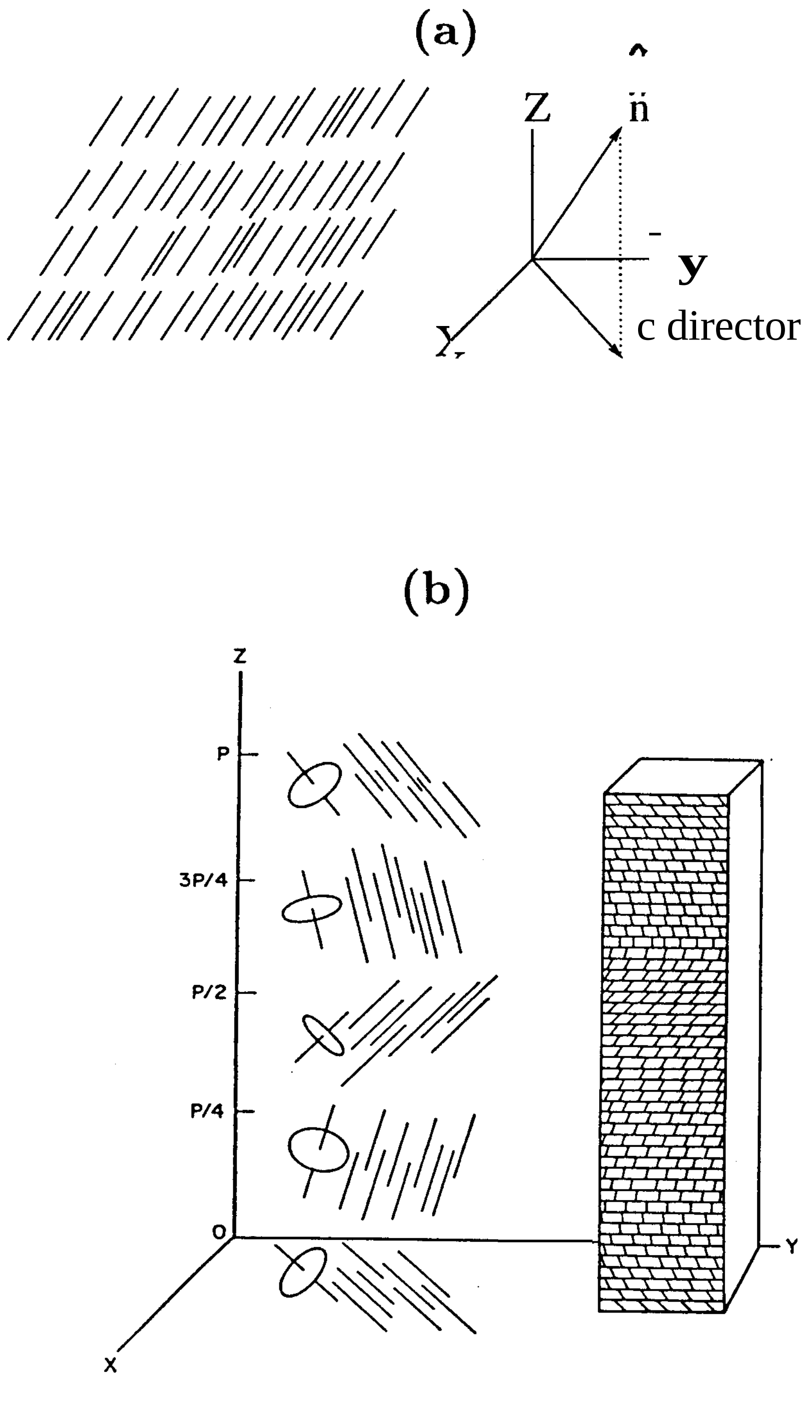

Figure 1.2: Schematic diagram of molecular arrangement in the (a) smectic C and (b) chiral smectic C phases.

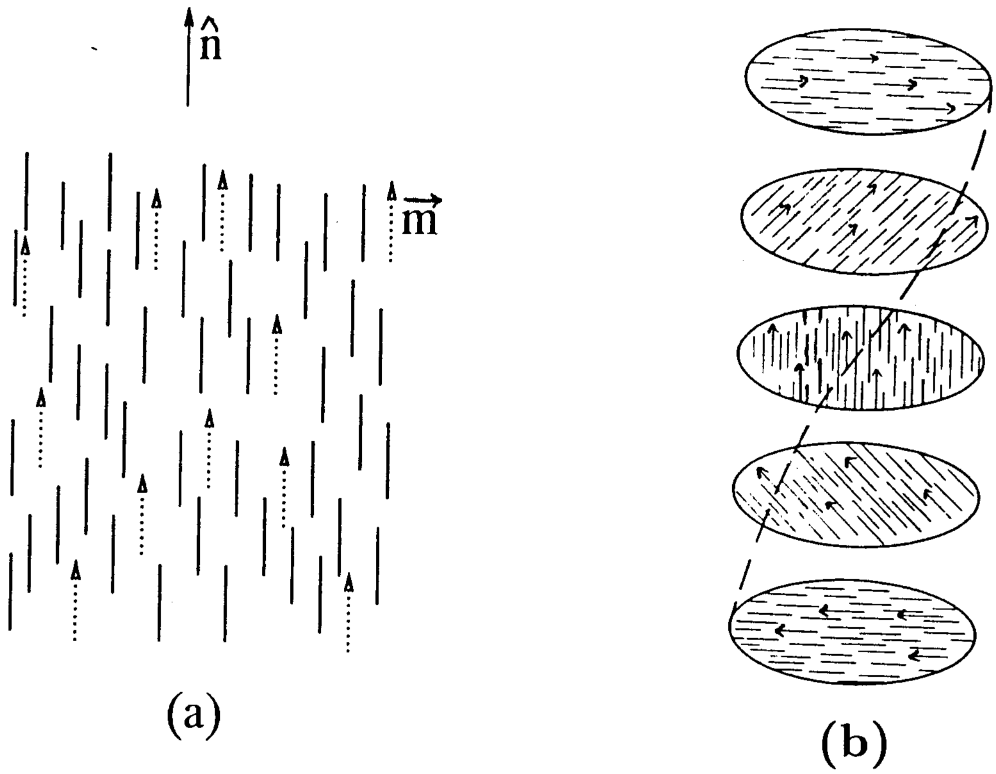

Figure 1.3: Schematic diagram of the molecular arrangement in the (a) ferronematic (magnetically doped nematic), (b) ferrocholesteric (magnetically doped cholesteric) phases. The arrow indicates the direction of magnetization.

of the ferromagnetic grains dispersed uniformly in the liquid crystal matrix. It is interesting to note that when the ferromagnetic grains are made up of transparent materials, like garnet, the inherent Faraday rotation of these grains can play a very important role in the optical properties of such liquid crystals.

Blue phases : It has been found that cholesteric phase with very small pitcli ($\leq 1\mu m$) can undergo phase transitions to thermodynamically stable phases before melting to the isotropic liquid in a very short temperature range ($\approx 1°$ C). These phases are known as blue phases [4]. They are of three types. Blue phase I and Blue phase II are in fact three dimensional network of line defects. Blue phase I has body centered cubic and Blue phase II has simple cubic structure. The structure of the Blue phase III (BP III) is not yet very well established.

1.2 Optics of chiral liquid crystals

The study on the light propagation in chiral liquid crystals have become very important since such liquid crystals are being commonly used in display and optical devices. They exhibit peculiar optical properties because of their twisted structure. A detailed review of the optical properties of chiral liquid crystals is given in [4].

Optically cholesterics can be described as an uniform rotation of a uniaxial index ellipsoid along the twist axis with the minor principal optical axis parallel to the twist axis. Similarly the structure Sc" can be optically characterized by a uniform rotation of the triaxial index ellipsoid, tilted at a constant angle θ, with respect to the twist axis. In the triaxial ellipsoid one of the principal directions can be taken to a good approximation along the long axis of the molecules, the second axis will be along the local two fold axis and the third in a direction perpendicular to these two. The Sc* phase is locally biaxial. Because of the apolarity of the director the optical periodicity of cholesteric medium corresponds to a π rotation of the director. However, the optical periodicity of Sc* phase is equal to the spatial periodicity P which represents a 2π rotation in the C director. For the light propagation in such a medium, the Maxwell's equations have to be solved with appropriate boundary conditions [15,16,17,18]. The two well known geometries to study the optical properties of the chiral liquid crystalline media are (i) Bragg mode and (ii) phase grating mode.

1.2.1 Light propagation in the Bragg mode

In this mode the light is incident parallel or at an angle ($< 90°$) to the twist axis. Here we assume the medium to be infinite in extent in the plane perpendicular to the twist axis and to have a thickness d along the twist axis. Figure 1.4a shows the geometry of light propagation in the Bragg mode.

The optical properties of cholesterics have been well studied in this mode [4]. The helical structure of the phase gives rise to many interesting optical properties, namely, high optical rotation, anomalous optical rotation near the selective Bragg reflections, non-Bragg reflections and anomalous transmission of the Bragg reflected wave when the medium is absorbing. In the case of normal incidence (light is incident parallel to the twist axis) cholesteric medium exhibits high optical rotation. The rotatory power of the medium can be as high as 10^3 degrees/mm and is very large compared to the crystal optical rotatory power which is of the order of few degrees/mm. The sign of the rotation changes across the reflection band. When the wavelength of incident light λ is much less than the pitch P then to a good approximation the cholesteric medium acts either as a pure rotator or as a pure retarder depending upon the relative values of pitch and birefringence of the medium [2]. In this thesis we have considered the optical properties of a ferrocholesteric which is a normal cholesteric with magnetic grains embedded in them. In this case we assume that the magnetization of the magnetic grains to be aligned parallel to the twist axis. The effect of the inherent Faraday rotation of the dispersed magnetic grains, when they are transparent, affect the optics of ferrocholesterics considerably in this limit.

A spectacular optical property of a cholesteric is the selective Bragg reflection that occurs when the wavelength of the incident light matches with the pitch of the medium. For an incident linearly polarized light parallel to the twist axis, it is found that one of the circularly polarized components is totally reflected while the other component passes unattenuated through the cholesteric medium. This is known as selective Bragg reflection. The reflected circular component has the same handedness as tliat of the cholesteric medium. The reflection band is centered around the wavelength $\lambda_o = \bar{n}P$ and has a width of AX $= \Delta nP$ [2], where $\bar{n}$ is the mean refractive index of the medium and Δn is the local birefringence of the cholesteric medium. Figure 1.4b shows a typical reflectance curve for circularly polarized lights at normal incidence. The eigenwaves inside the cholesteric medium are right and left circularly polarized waves. In the reflection band, the interference of these eigenwaves (forward propagating and backward propagating) gives rise to a standing wave that is locally linearly polarized. With linear dichroism in the cholesteric

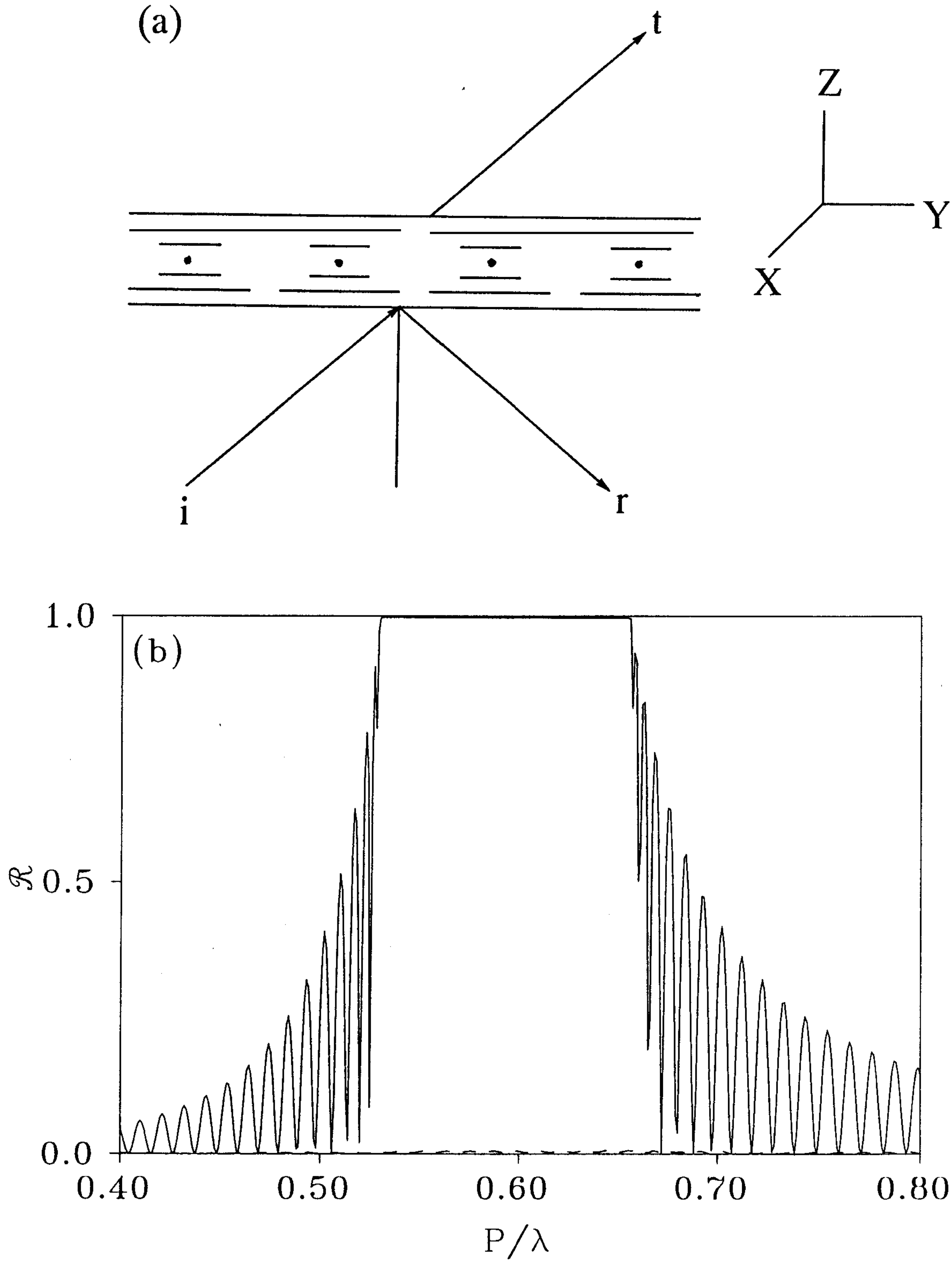

Figure 1.4: (a) Schematic diagram of light propagation in Bragg mode. i, r, t represents the incident, reflected and transmitted waves respectively. (b) Reflection curve for the right circularly polarized light (continuous line) and for the left circularly polarized light (dashed line) incident normally on a right handed cholesteric liquid crystal in the Bragg mode .

medium, the Bragg reflected circular wave gets anomalously transmitted at the short wavelength side of the Bragg band as compared to the unreflected circularly polarized wave that experiences only the average absorption of the medium. This anomalous transmission is the optical analogue of the Borrmann effect in X-rays [19].

At oblique incidence of light we get higher order Bragg reflections. Each reflection band splits into three sub-bands. The reflected light in the central sub-band is insensitive to the polarization of the incident wave. It is called the non-Bragg band. In this region both the eigenmodes inside the medium are attenuated and the reflectivity becomes unity [20,21]. A chapter in this thesis is devoted to study anomalous transmission at oblique incidence in the first and higher order reflection bands. The effect of absorption on the non-Bragg reflection band has also been investigated.

1.2.2 Light propagation in the phase grating mode

In this mode light is incident perpendicular to the twist axis. The schematic diagram of the light propagation in the phase grating mode is shown in figure 1.5. Here we assume that the medium is infinite in extent along the twist axis and has a finite thickness d in the propagation direction of the incident light. For a polarized light incident normal to twist axis, the medium acts as a one dimensional phase grating.

When a plane wavefront of polarized light is incident normal to the twist axis it experiences a periodic change in the refractive index. In cholesteric and Sc* liquid crystals the phase modulation is due to a continuous change in the local refractive

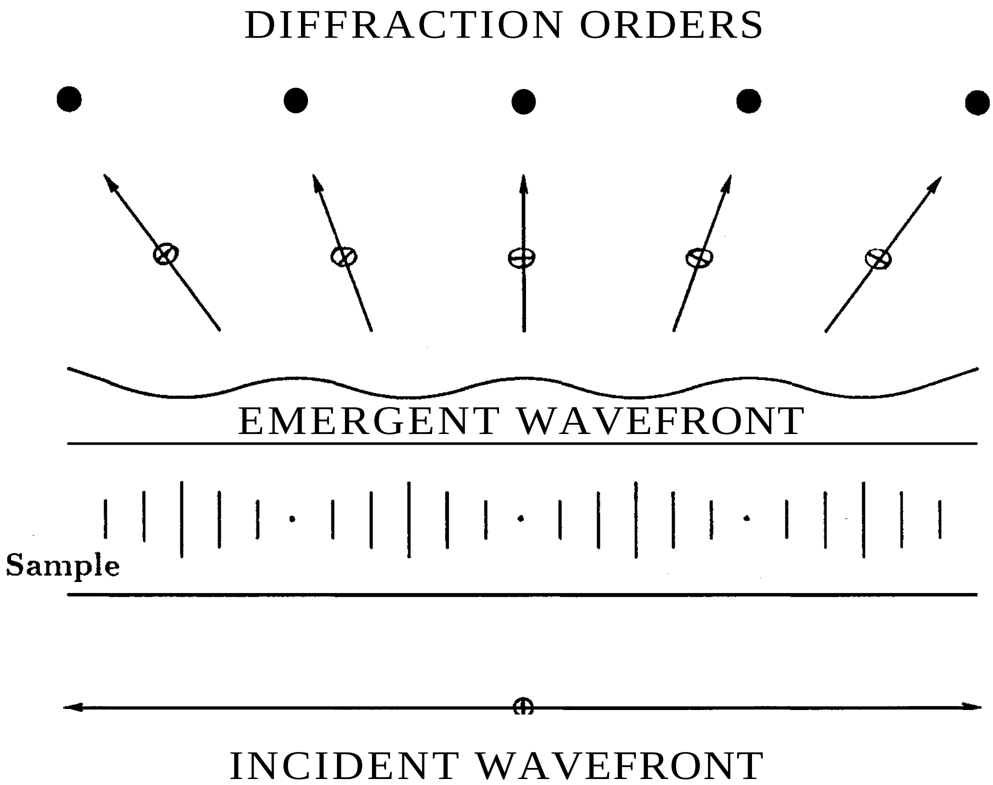

Figure 1.5: Schematic diagram of light propagation in the phase grating mode. The incident wave is linearly polarized with its electric vector perpendicular to the twist axis.

index of the medium arising out of their twisted structure. The phase grating effect can also be found in some nematic liquid crystals aligned in suitable geometry, wherein the application of a suitable electric or magnetic field induces a periodic structure.

When refractive index variations and grating thicknesses are small, we can ignore internal diffractions and an incident plane wavefront emerges out of the sample as a periodically phase corrugated wavefront resulting in the optical diffraction. Raman and Nath were first to solve the problem of phase grating in the context of ultrasonic diffraction of light [16]. In the Raman and Nath (RN) theory the diffraction pattern can be calculated under two assumptions: (i) wavelength of light is much less than the wavelength of the phase fluctuations on the wavefront, (ii) the amplitude of phase fluctuations is much less than the wavelength of the phase fluctuations. Suresh et.al. [8] have developed a generalized RN theory to compute the diffraction pattern for cholesteric and Sc* phases. We mentioned earlier that the cholesteric and Sc* have different optical periodicities. This difference in the periodicity gives rise to extra diffraction orders in Sc* phase compared to the cholesteric. Also for Sc* there is a diffraction for any azimuth of the incident linear polarized light unlike in cholesterics wherein we get diffraction only when the electric vector of the incident light has a component perpendicular to the twist axis. Experiments have been performed in this mode on binary cholesteric mixture by Sackmann et.al. [5]. They used the diffraction pattern to study the pitch of the phase. Tanguay et.al. [22] used a nematic liquid crystal under electric field to study the polarization features of the diffraction pattern of the modulated structure. In this thesis we present a detailed experimental and theoretical study of the intensity and polarization features of the diffracted light in the Sc* liquid crystal in the phase grating mode. We have also theoretically investigated the effect of inherent Faraday rotation on the diffracted light from a ferrocholesteric aligned in the phase grating mode.

1.3 Optics of a quasi-periodic liquid crystalline medium

In recent times, optics of quasi-periodic medium has attracted a lot of attention. Properties like self-similarity in the reflection band [23], localization of light [23,24] and power law transmittance [25] are some of the features associated with these structures. Todate these studies were made only on the isotropic dielectric structures [26,25,24]. With these views in mind, in chapter 6, we have studied light propagation in both Bragg and phase grating mode in an anisotropic quasi-periodic structure taking the example of a quasi-periodic cholesteric. This study is of some relevance to the elucidation of the structure of the BP III which is suspected to be quasicrystalline [27,28].

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