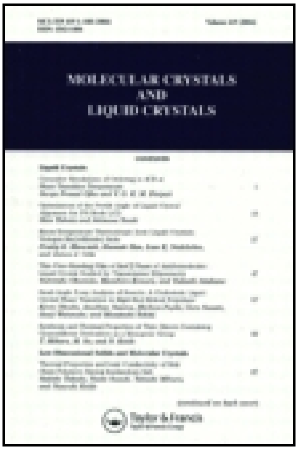

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Influence of Cholesteric Bragg Reflection on Spontaneous Emission from the Inside of the Helical Structure

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Influence of Cholesteric Bragg Reflection on Spontaneous Emission from the Inside of the Helical Structure

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Spontaneous emission from a luminescent center doped in the periodic structure of a cholesteric liquid crystal is experimentally investigated. The characteristic Bragg reflection for the light emitted from the inside of the helical structure is observed as a deep dip in the emission spectrum, when the emission band is wider than the reflection band. The dip position identical to the optical pitch shifts as a function of temperature. The luminescence intensity decay profiles, however, show no meaningful difference over two decades between the cases that the Bragg condition is satisfied or not, contrary to the experimental observation by Dreher and Schomburg.

INTRODUCTION

It is well known that one circularly polarized light almost identical in shape to a cholesteric helix is strongly Bragg reflected while the other with opposite handedness can be transmitted if light is incident from outside to the medium along the helical axis. Such a Bragg reflection also takes place for the light incident obliquely to the helical axis. In other words, there exist forbidden gaps (opacity bands) in the dispersion relation for the optical eigenmodes propagating in the spatially periodic helical structure of cholesteric liquid crystals.[1,2] This may mean that luminescent centers in cholesteric liquid crystals cannot emit the light corresponding to the optical eigenmodes in the forbidden gaps. The present study was motivated by the following simple question. Does the existence of such forbidden gaps affect the transition probability of luminescence, resulting in the prolongation of its decay time?

The radiative decay time of a luminescent center is not determined by the state of the center alone but depends on the state of the radiation field. Actually, Kuhn[3] showed that the decay time of luminescence of a molecule in front of a metal mirror depends markedly on its distance from the mirror. Moreover, Dreher and Schomburg[4] experimentally investigated the spontaneous emission of oriented molecules in the helical structure of a cholesteric liquid crystal. They found that the decay time is markedly lengthened when the structural forbidden gap (the characteristic Bragg reflection band) coincides with the emission band.

This problem appears to be important and interesting, and moreover we have experimentally studied[7] the dispersion relation for the optical eigenmodes propagating in a cholesteric liquid crystal, N-p-etoxybenzylidene-p-2-methylbutylaniline (EBMBA), which has wide forbidden gaps due to a large local birefringence; hence we have tried to confirm Dreher and Schomburg's result using EBMBA. Because of its wide forbidden gaps, we could expect significant prolongation of the luminescence decay time. The results will be reported in the following, though negative; no prolongation was confirmed in our experiments.

2. EXPERIMENTAL PROCEDURE

2.1 Sample preparation

Three kinds of cholesterics used are listed in Table I. Cholesterol derivatives, Ch N and Ch A, were purchased from Tokyo Kasei Kogyo Co. Ltd., and cyanobiphenyls, CB15 and 7OCB, from BDH Chemicals Ltd. EBMBA was synthesized by a modified version of the method reported by Dolphin et al.[8] Luminescent guest molecule, DH, Eu or ANB, was dissolved in a host cholesteric with the concentration of about 0.3 wt%. The monodomain cholesteric samples were prepared between two microscope slides or two rectangular prisms separated typically by 25 μm spacer. The surfaces were treated with polyvinyl alcohol and rubbed in one direction back and forth.

TABLE I

List of samples

		Luminescent guest molecules	Decay time	Bragg reflection peak at RT	Reflection width	Emission band width
1	80% Ch N & 20% Ch A	DH	~7 ns	460 nm (at 40°C)	~ 20 nm	~100 nm
2-A	25.4% CB15 & 74.3% 7OCB	Eu	~400 μs	1000 nm	~100 nm	~10 nm
2-B	38.4% CB15 & 61.3% 7OCB			640 nm		
2-C	45.4% CB15 & 54.3% 7OCB			520 nm		
3-A	racemic EBMBA	ANB	2.2 ns	———	~100 nm	~100 nm
3-B	64.9% active and 35.1% racemic EBMBA			550 nm		
3-C	83% active and 17% racemic EBMBA			357 nm		

Abbreviation:
Ch N; cholesteryl*nonanoate*
Ch A; cholesterylacetate
CB15; 4-(2-methylbutyl)-4′-cyanobiphenyl
7OCB; 4-cyano-4′-n-heptoxybiphenyl
EBMBA; N-p-etoxybenzylidene-p-2-methylbutylaniline
DH; 1-6-diphenyl-1-3-5-hexatriene
Eu; Tris (heptafluorobutanoylpivaloylmethanato)europium
ANB; 4-amino-4′-nitrobiphenyl

2.2 Experimental setup

The emission spectra were observed, unless otherwise stated, from the direction along the helical axis, using the samples prepared between two microscope slides. A light source was an Hg lamp. Two monochromators (Nikon G-250) were used; one was for obtaining exciting light and the other for analyzing luminescent light. Temperature was controlled within ±0.1°C in an oven if necessary.

Two separate setups were used for measuring the decay time. The observation direction and the temperature control in both setups were similar to those used in obtaining the emission spectra. For the decay time of the order of 100 μsec, the time dependence of the luminescence was detected by a photomultiplier (HPK-R446) after exciting the sample by a Xe flash lamp of duration 10 μsec. The signal was stored in a transient memory (Kawasaki Electronica, MR-50E) and accumulated by a microcomputer (Hitachi, HMCS-6800) to improve the signal/noise ratio. The decay time of the order of nanosecond was measured by a nanosecond fluorescence spectrometer (Ortec 9200) combined with a multichannel analyzer (Camberra 8100) and a microcomputer (Fujitsu FM8), based on a time-correlated single-photon counting technique. Average number of photons counted was in the range between 20000 and 50000.

3. EXPERIMENTAL RESULTS

3.1 Emission spectra

Emission spectra for the sample 1 in Table I are shown in Figure 1. The width of the characteristic Bragg reflection band of cholesterol derivatives is about 20 nm and the emission band width of DH is about 100 nm as listed in Table I. Therefore the reflection band is observed as a deep dip as shown in Figure 1. With increasing temperature the dip shifts toward the shorter wavelength side in accordance with the temperature dependence of the helical pitch. Such a shift of the dip position was also observed by measuring the spectra obliquely as shown in Figure 2. Note that the reflection band shifts toward the shorter wavelength side with increasing angle of incidence.[5,6,7]

As for the sample 2, the emission band width of Eu is much narrower than the width of the reflection band as shown in Table I and Figure 3. In the emission spectrum, an increase in the shorter wavelength side is due to the luminescence of the host liquid crystal. Figure

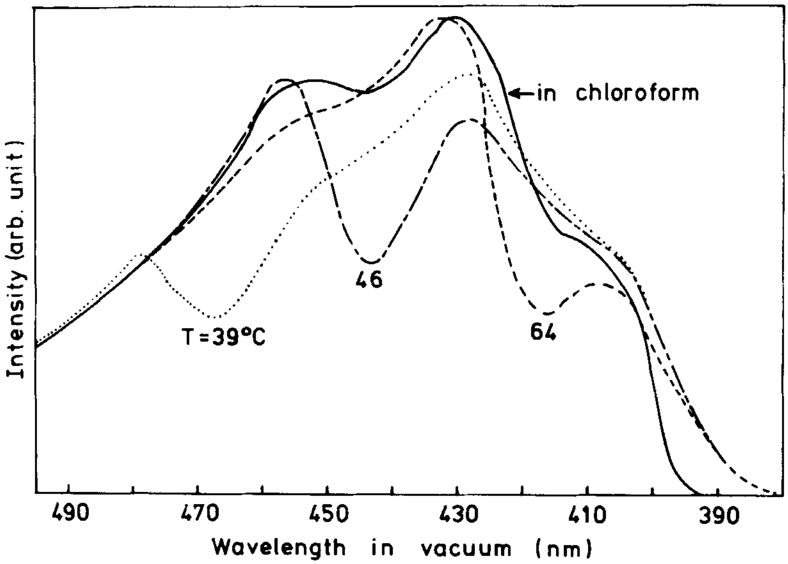

FIGURE 1 Emission spectra for the sample 1 at various temperatures.

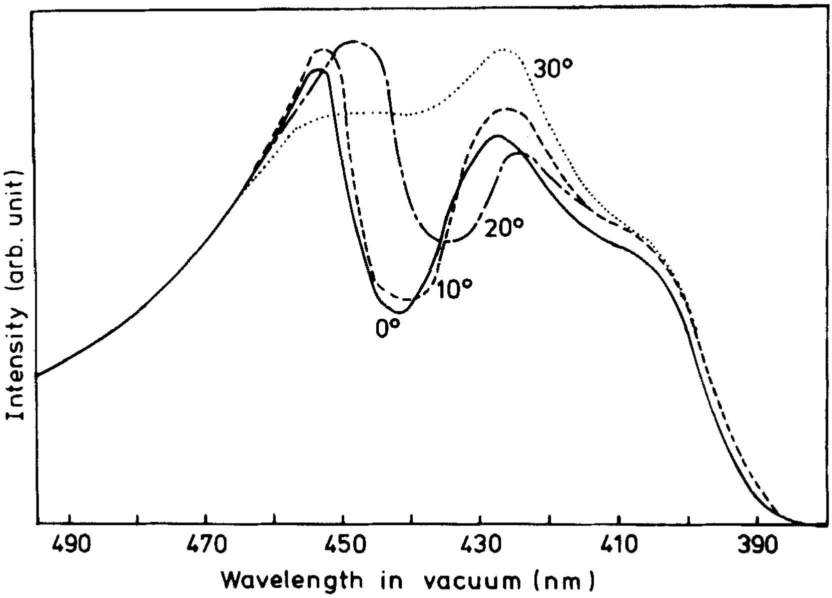

FIGURE 2 Emission spectra for the sample 1 observed from different directions relative to the helical axis at 46°C.

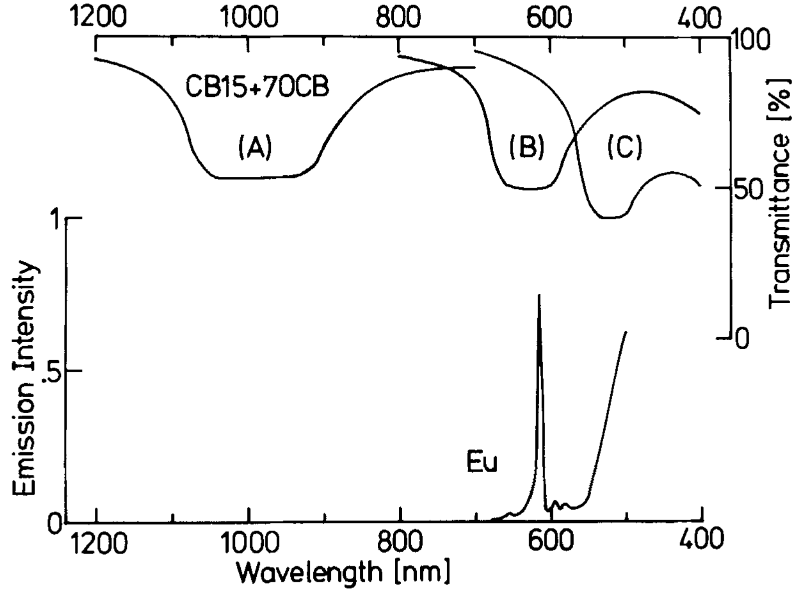

FIGURE 3 Transmittance and emission spectra for the sample 2 at room temperature.

4 shows that the emission intensity is almost half the others when the emission band is covered with the reflection band as in the sample 2-B. Thus the emission intensity for a certain direction is really influenced by the reflection band.

3.2 Decay times

To observe the influence of the forbidden gap on the decay time effectively, the reflection band is desirable to be wide, so that the solid angle in which the light cannot propagate becomes large, while the emission band is desirable to be narrow so as to be well covered by the reflection band. In the sense, the sample 2 was first chosen for the decay time measurements. As shown in Figure 3, when observed from the direction along the helical axis, the sample 2-B has a reflection at about 650 nm which is close to the emission band. The optical pitch of the sample 2-A is about 1000 nm but the reflection band coincides with the emission band for the light propagating along the direction forming an angle of about 50° with the helical axis. Therefore some differences in the decay profiles were expected among the samples 2-A, 2-B and 2-C. However the observed decay curves

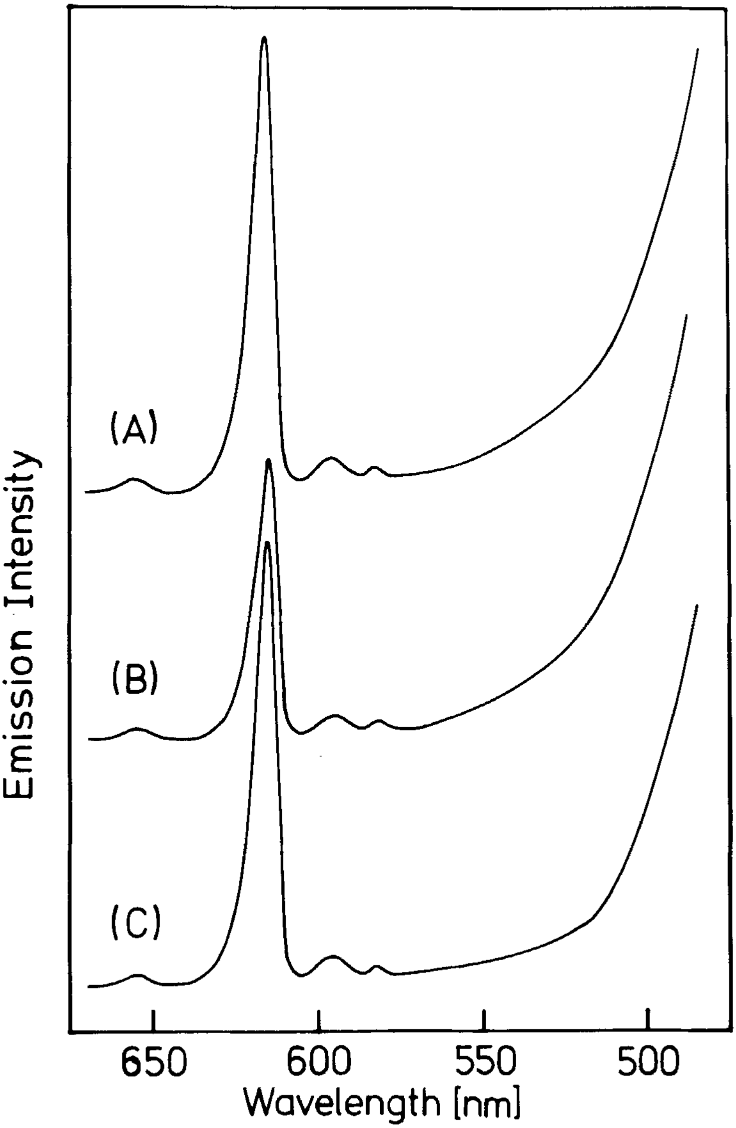

FIGURE 4 Emission spectra for the sample 2 at room temperature.

reveal no detectable difference over two decades of intensity change as shown in Figure 5.

It is well known that the director of liquid crystals thermally fluctuates, resulting in strong light scattering. Therefore it may be pos-

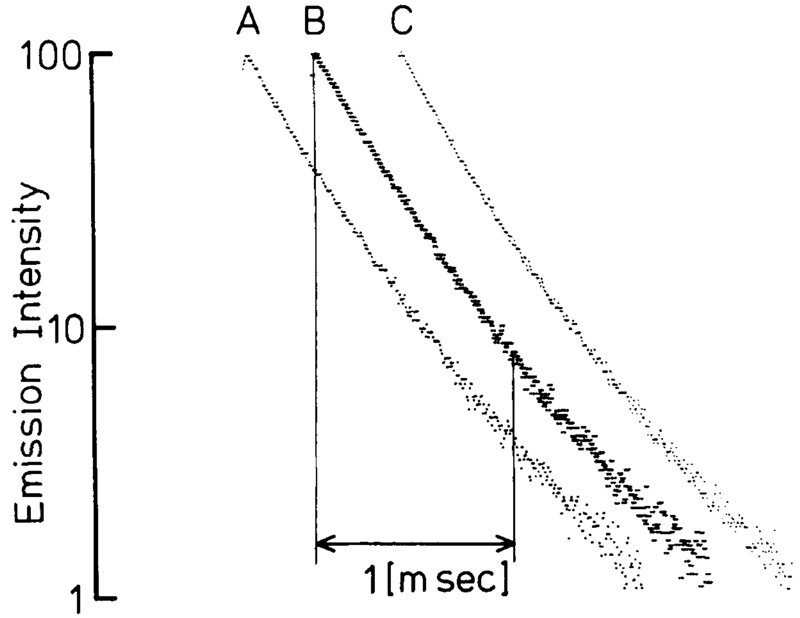

FIGURE 5 Logarithmic plot of emission intensity of the sample 2 against time.

sible that the luminescent light virtually emitted to the direction along which light cannot propagate is subjected to the scattering to other directions along which light can propagate. In the case of the sample 2, the decay time is relatively long (~400 μsec) and is comparable to the relaxation time of the director fluctuations. To eliminate the effect of the director fluctuations, the ideal sample should emit a luminescence of short lived as compared with the relaxation time of the director fluctuation. In the sense, the sample 3 was chosen though the emission band width is relatively wide.

The transmittance and the emission spectra for the sample 3-B are shown in Figure 6. Only the sample 3-B is expected to suffer the influence of the forbidden gap; the sample 3-C has the characteristic reflection band in shorter wavelength side than the emission band, and the sample 3-A is nematic.

Contrary to the expectation, no difference in decay curves can be seen over two decades of the intensity change among the three samples 3-A, B and C as shown in Figure 7. The decay curves may not show the true decay, since the duration of exciting light pulse used is not narrow enough as indicated in Figure 7. However the difference should be observed if any. Thus we experimentally showed that the

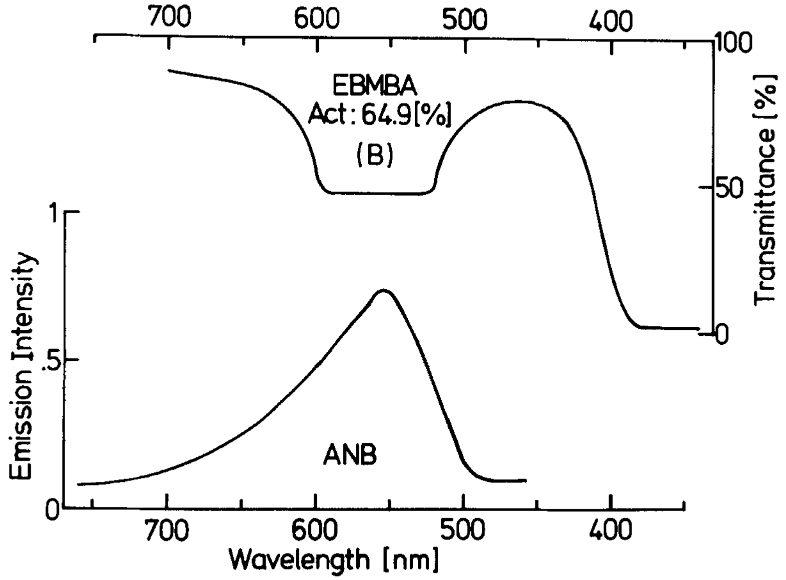

FIGURE 6 Transmittance and emission spectra for the sample 3-B at room temperature.

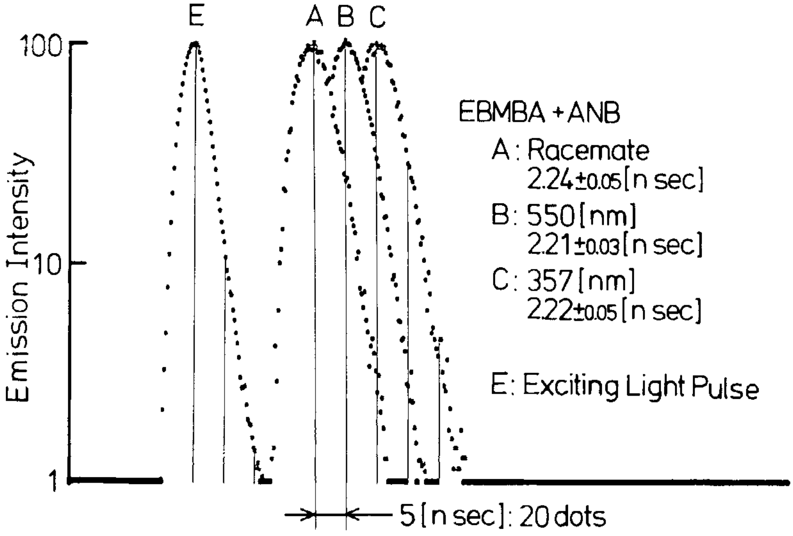

FIGURE 7 Logarithmic plot of emission intensity of the sample 3 against time. The shape of the exciting light pulse used is also plotted.

difference cannot be observed in the decay profiles over two decades between samples with and without the reflection band.

4. DISCUSSION

Let us roughly estimate the amount of light emitted into the forbidden gap. In case of EBMBA, which has large dielectric anisotropy $\alpha = (\epsilon_{\parallel} - \epsilon_{\perp})/(\epsilon_{\parallel} + \epsilon_{\perp}) = 0.144$ and has consequently the wide reflection band, the light propagating along the direction within about ±15° from the helical axis suffers reflection.[7] Therefore the solid angle of the region where the reflection takes place is only $4\pi(3.4 \times 10^{-2})$ sr. There exist four optical eigenmodes, two of which may be propagation modes. Therefore only 1.7% of light would be emitted into the forbidden gap. The angular distribution of the luminescence may increase this percentage, but the spatial distribution of the luminescent impurity inside the cell and the finite width of the emission band may decrease it further. If we use a mixture of cholesterol derivatives as the host cholesteric as Dreher and Schomburg[4] used, the effect amounts to less than 0.1% because of the small dielectric anisotropy, $\alpha = 0.03$.

They observed a luminescence from tetraphene, whose emission band consists of three subbands corresponding to 0-0, 0-1 and 0-2 phonon transitions. Decay time measurements were performed from the direction along the helical axis, where the 0-1 subband coincides with the reflection band. They claimed that the decay time of the 0-1 band is prolonged as compared with that of the 0-0 and 0-2 bands. This observation is slightly puzzling because the decay time is usually considered to reflect the number of the molecules in the excited state and hence all the subbands, 0-0, 0-1 and 0-2, are expected to have the same decay profile. Moreover, the influence of the helical structure was so large that the maximum prolongation they observed was 66%. Because of the differing decay profiles for the different phonon transitions as well as the remarkably large prolongation, they suggested the presence of the "dynamic state" predicted by Bycov;[9] it was considered to be formed by the molecular states and the electromagnetic field of the standing waves in the forbidden gap. Unfortunately, we could not observe any prolongation of the decay time notwithstanding our experimental condition better than Dreher and Schomburg's in the accuracy of measurements as well as in the selection of samples; their decay profile was obtained by a photograph of an oscilloscope record, and their host liquid crystal was a mixture of cholesterol derivatives. So far we do not know the reason why the prolongation was observed in their system, but not in our system. We may ought to increase the accuracy of the experiment for a definite confirmation of the change in the decay profile.

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