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On the Origin of Second Harmonic Generation of Light in Liquid Crystals†

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Abstract—Second Harmonic Generation of light (SHG) is used as a probe to study the structure of the nematic, cholesteric or smectic mesophases of various liquid crystals, with non centro-symmetric molecules. In one case (cholesteryl 2-(2-ethoxy ethoxy) ethyl carbonate) where SHG has already been reported, it is shown that SHG occurs in the crystalline rather than the mesomorphic phase. In all cases, no evidence is found of any SHG in any mesophase. Consequently, these are probably centrosymmetric by compensation, as is the normal liquid phase.

I. Introduction

The development of high power lasers has led, in the recent years, to the observation of non-linear optical properties of many materials.[1] One of the lowest order non-linear effects is the second harmonic generation of light (SHG) where two photons of a laser beam combine to produce one photon at twice the energy. In the electric dipole approximation, this effect can only occur in a medium which lacks a center of inversion. In this process, the flow of energy between the laser and the harmonic waves depends on their phase relationship.[2] It is of great practical importance to achieve the so called "phase matching" condition.[2] The natural dispersion of the optical index between the two beams can be compensated by the use of birefringent media and suitable polarizations of light beams.[3,4]

The first motivation for the investigation of SHG in liquid crystals has been to take advantage of their large possible birefringence[6]

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to achieve the phase matching condition: linear birefringence on macroscopically oriented nematic materials, or circular birefringence[5] for cholesteric liquid crystals. However, the observation of a large SHG of light from a mesomorphic phase would have a more fundamental interest. A large SHG would prove that the medium lacks a center of inversion (is piezoelectric) on the scale of an optical wavelength. It could show, for instance, that inside "swarms"[6] the non-centrosymmetric molecules of a nematic liquid crystal keep statistically a parallel orientation, rather than a close packed antiparallel arrangement with no large scale piezoelectric symmetry. This kind of structural information, complementary to the X-ray studies, cannot be derived from linear optical experiments.

The recent observation of SHG in cholesteryl 2-(2-ethoxy-ethoxy) ethyl carbonate (CEC) by Freund and Rentzepis[7] seems to have opened a promising way to study the structure of mesomorphic materials. In this paper, we report on our observations of SHG of light in various liquid crystals. We first show that in CEC, SHG is initiated by ordinary micro-crystals floating in the bulk of the mesomorphic material. The particular melting process of these crystals can simulate a mesomorphic to isotropic phase transition. Investigations on other nematic, cholesteric or smectic liquid crystals, also reveal no SHG in the mesomorphic arrangement. It is concluded that, as far as SHG of light is concerned, the liquid crystals behave more like liquids than like crystals. Some preliminary results have been reported.[8]

II. Origin of SHG of light in cholesteryl 2-(2-ethoxy ethoxy) ethyl carbonate (CEC)

(a) *Physical properties of CEC*

The sample was obtained from Eastman Kodak Company, Distillation Products Industry. Quantitative carbon hydrogen analysis is correct to 99.8% . Chromatography shows the presence of traces of two unidentified impurities. The material is a viscous liquid at room temperature, which absorbs 80% of a light beam at 3470 Å (second harmonic wave length of the ruby laser) in one cm path length. It is, however, transparent for wavelengths larger than 4000 Å. For all temperatures lower than $T_c = 48.5°$C, a layer of the Grandjean plane cholesteric structure[6] grows slowly on the free surface of the material. This texture is identified by the observation under a microscope of the Grandjean plane edges, and by its large rotatory power (~ 3 to 8.10^3 degree/mm in the visible). The equidistance between Grandjean planes versus temperature has been measured, using a Bragg-type light scattering experiment.[9]

The rotatory power of the bulk liquid is normal. The specific rotation is lefthanded, and amounts to 2°/cm at 6943 Å and 5° at 3470 Å, with no significant temperature dependence from 18°C to 60°C. The sample viscosity, measured with a Cannon-Fersske viscometer, presented some temperature hysteresis and the data were not reproducible. However, one could always observe a bump in the viscosity at $T = T_c$, in agreement with the known behavior of liquid crystals.[8] Spontaneous and stimulated Brillouin light scattering, measured in collaboration with D. V. L. G. Narasimha Rao,[10] shows a dispersion in the hypersound velocity around T_c. We, therefore, believe that the bulk consists of many small scale ordered cholesteric domains, generally smaller in size than the wavelengths of light and of the Brillouin sound waves observed in the experiment (0.2μ).

When a drop of fresh sample at room temperature is viewed under a microscope between crossed polarizers, one can see small birefringent leaflets (Fig. 1). These leaflets are real crystals, as shown below. Their sizes vary from a few μ to some 80μ. Their density is slightly larger than that of the bulk. Their birefringence is large. A retardation of ninety degrees for blue light occurs in a thickness of 3–5 microns. Their optical axes are often close to their symmetry axes and they may be biaxial. Isolated by filtration, the leaflets show the same infrared spectra and chromatograms as the liquid, with the presence of the same two unidentified impurities. Figure 2 is the Debye-Scherrer diagram of X-ray analysis of the filtrated residue. Note that there are more than 20 sharp lines with parameters from 2 to 10 Å, the upper limit imposed by our X-ray camera. These rings are typical of a molecular crystal, and have never been observed in any mesomorphic material. The leaflets are, therefore, ordinary crystals of CEC, belonging to a piezoelectric class since they can produce SHG, as shown later.

The crystals grow according to two different processes. For all temperatures T lower than $T_M = 32.5°\mathrm{C}$, a focal conic mesomorphic structure appears first. Its nature (smectic or cholesteric)

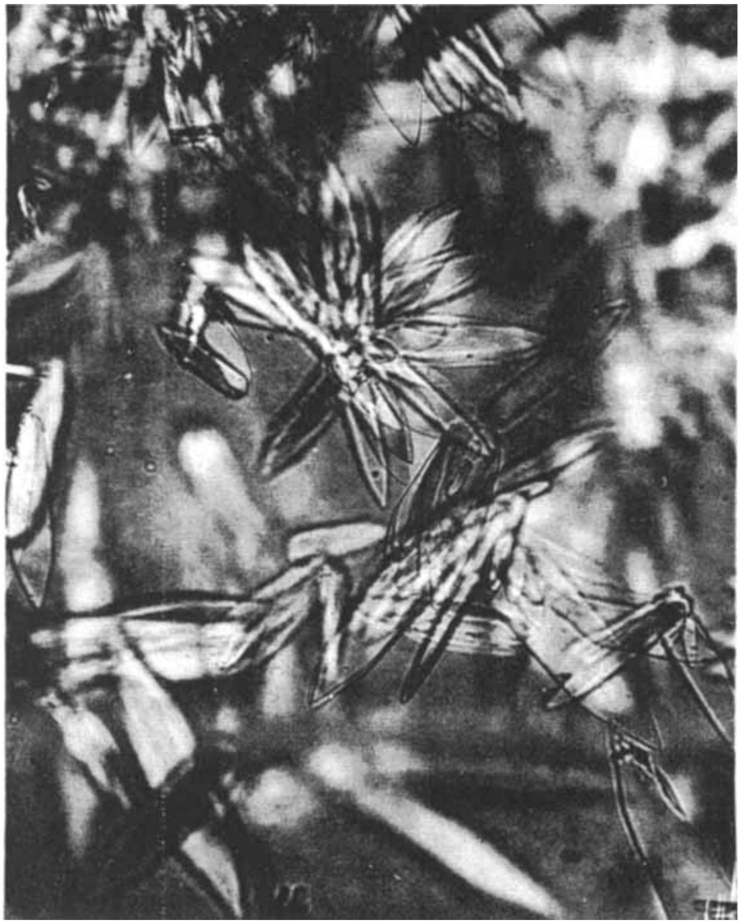
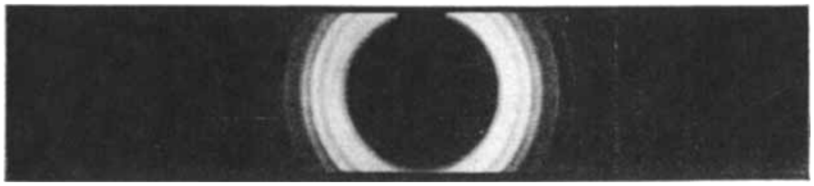
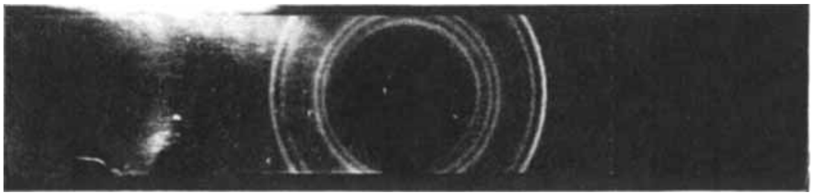


Figure 1. Clusters of crystalline leaflets of cholesteryl 2-(2-ethoxy ethoxy) ethyl carbonate (CEC), under cross-polarized microscope.

has not been elucidated. Subsequently the crystal growth goes over into a pseudomorphic arrangement, giving rise to the leaflets which separate in the bulk, after some weeks. Another process occurs when T is just equal to T_M. In this case the crystals grow directly from the bulk, in their final shape, in a much shorter time (one day or so). These processes have already been observed by Friedel[11] on other mesomorphic compounds. Above T_M the crystals begin to melt slowly, as we shall discuss later.



(a) K_α Cr



(b) K_α Cu

Figure 2. X-ray powder diagrams of CEC crystals; (a) K_α Cr line, (b) K_α Cu line; observed parameters from 1.88 Å to 10.35 Å (maximum allowed by the camera).

(b) *SHG of light in CEC*

Let us first review the work of Freund and Rentzepis.[7] They used a conventional technique. Shining a ruby laser beam on a bulk sample, they made the following observations: (a) the sample emits a monochromatic radiation at twice the frequency of the laser light along the laser beam; (b) the intensity of this emission varies as the square of the laser power; (c) the emission is depolarized; (d) SHG disappears above the mesomorphic to isotropic temperature $T_c = 48.5°\text{C}$. Observations (a) and (b) are characteristic of all coherent SHG and observation (d) was their only reason to conclude that the SH signal was generated in the liquid crystal mesophase, the nature of which was not precisely stated. Our measurements show, in fact, that SHG was initiated in real crystals floating in the bulk. This result explains the point (c), and is compatible with (d) as we shall see later.

We made most of our measurements on CEC in a one centimeter long cell with an H_2 Raman laser[12] at 9755 Å wavelength. This has

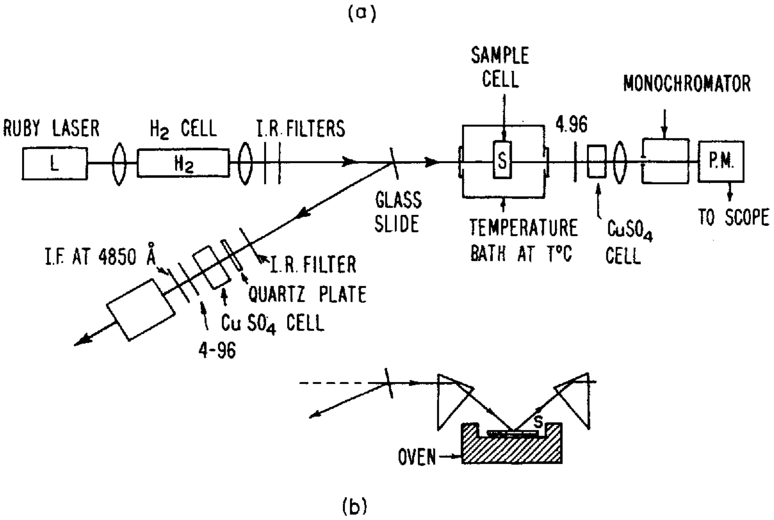


Figure 3. Experimental apparatus for Second Harmonic Generation of light in liquid crystals: (a) in transmission, (b) in diffuse reflection.

the advantage that the sample is more transparent at the corresponding SH frequency. Some of our early experiments were carried out with a ruby laser at 6943 Å, with essentially the same results. We consider these results less precise because of the increased absorption of the SHG. The experimental setup is shown on Fig. 3(a). The light beam of a Q-switched ruby laser (20 MW output power) is focused in the center of a 80 cm H_2 cell (500 psi) by a 50 cm focal length lens. A second symmetrical lens reproduces a parallel beam; infrared filters allow only the first stokes Raman line of H_2 at 9755 Å, stimulated in the cell, to hit the sample. Eight per cent of the incident power is sent to a monitor channel, generating SH in a quartz plate, eliminating problems due to laser fluctuations[13]. The sample cell is immersed in a thermostat which stabilizes the temperature to better than 0.5°C. A Corning CS 4–96 filter and a $CuSO_4$ cell block the fundamental light. The SH signal is collected on the slit of a monochromator and detected by a photo-multiplier. A dual beam oscilloscope displays the signals for both channels to check the time correlation of the SH from CEC and quartz. We can detect signals as low as 4 orders of magnitude below the one from quartz; in practice, for the weakest signal observed, the signal-to-noise ratio was better than 10:1.

With this arrangement, we have repeated the Freund and Rentzepis[7] experiment. We have established a complete correlation between the depolarized second harmonic light and the presence of crystals in the cell. If the crystals are left to settle on the bottom of the cell, for instance, the liquid crystal does not produce any SH. After agitation of the sediment, the crystals reappear in the field of the laser beam and so does the SHG. The harmonic intensity increases with the concentration of crystals. We have prepared different samples with a Grandjean cholesteric texture oriented surface: only those which contain crystals in addition to the cholesteric texture gave SHG. As long as there remained some crystals in the sample, SHG persisted, even beyond T_c where the cholesteric texture is destroyed. The SH intensity was the same for two samples of equal thickness, equal density of crystals, but one having a Grandjean layer and the other none. This shows that the Grandjean texture gives no contribution to SHG.

It remains to explain the disappearance of SHG above T_c. We start with a fresh sample containing crystals and we increase the temperature T of the cell. The SH intensity is given in Fig. 4(A) which shows that the signal vanishes above T_c. However, when decreasing T, one cannot find the signal back for $T < T_c$, although we know that the Cholesteric→Isotropic transition in CEC is reversible. Under the microscope, one sees that all the crystals have melted.

We have studied the melting process of the crystals by recording the SH intensity as a function of time, for samples held at different

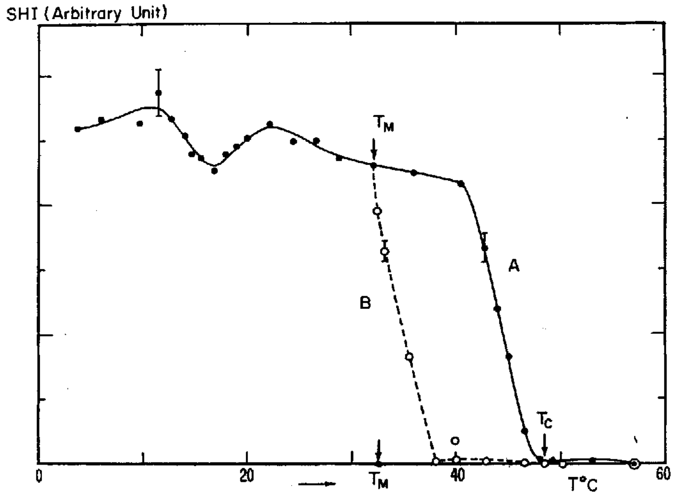


Figure 4. Intensity of Second Harmonic light, versus temperature T of the liquid crystal CEC; (A) on a single sample, at rapid increasing temperature, (B) on different samples at constant temperatures, after 18 hours; T_c and T_M are the cholesteric→isotropic and the melting temperatures.

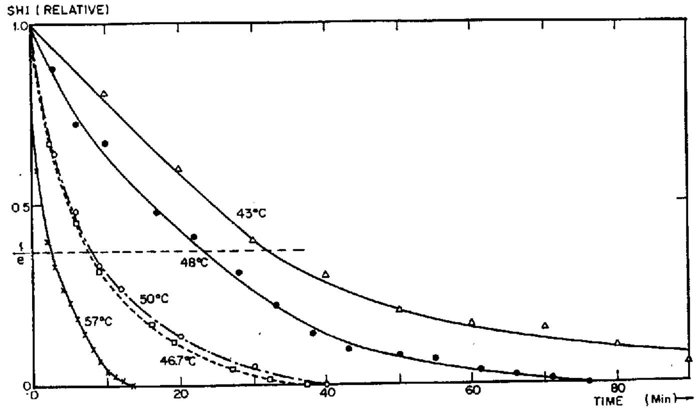


Figure 5. Normalized SH intensity as a function of time, for different CEC samples at constant temperatures. The 1/e line defines the melting time τ of the CEC crystals.

constant temperatures, normalizing the initial signal. For all samples kept above $T_M = 32.5°C$, we observe under the microscope the gradual melting of the crystals and the SH intensity decreases exponentially to zero. The decay is shown on Fig. 5 for various temperatures. Note that even above T_c, it takes a finite

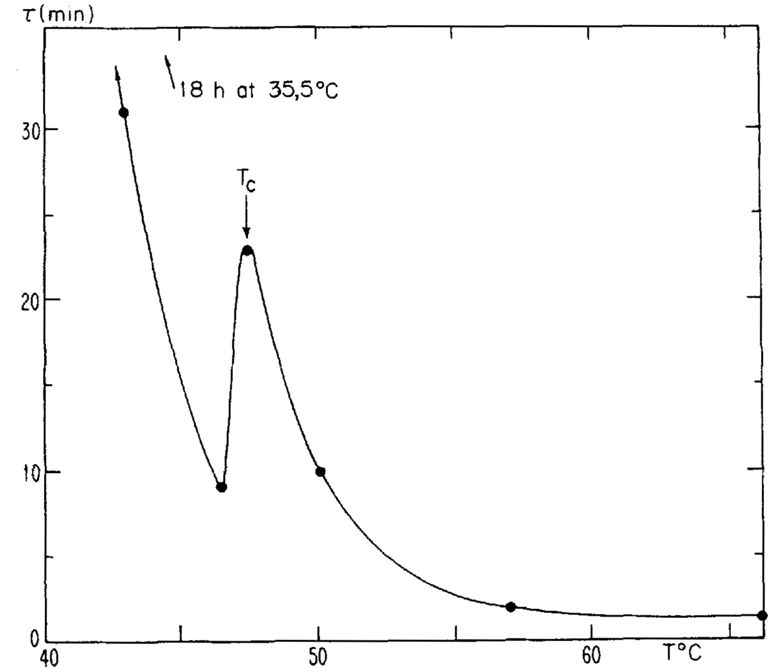


Figure 6. Melting time τ of the CEC crystals versus temperature. Note the peak at $T = T_c$.

amount of time for the signal to vanish, although the cholesteric to isotropic transition is known to be sharp. The variation of the time constant τ versus T is shown by Fig. 6. The interesting feature is the noticeable peaking of τ at $T = T_c$. This corresponds to the anomalous behavior of the viscosity at the transition temperature.

One can thus understand why, on a first temperature run as in Fig. 4(A) the SH signal vanishes beyond T_c. It takes about 5 minutes to measure each point so that, above T_c, the melting time τ becomes shorter than the interval between two measurements. If the intensity of the harmonic generation is measured for a sample that has been kept at each fixed temperature for 18 hours, one obtains the dotted curve (B) (Fig. 4). Note that the crystals have practically melted above 37°C, which is well under T_c.

After melting of the crystals, the SH signal can be kept vanishingly small for weeks, by leaving T above T_M. On the other hand, a sample initially without crystals will show SHG if kept below T_M for several days. At the same time, crystals reappear in the bulk according to the already described process.

III. Investigation of SHG in various mesomorphic materials

In some nematic liquid crystals, say p-azoxyanisole (AA), a random rotation of the molecule around its main axis, if allowed, is sufficient to make the mesomorphic phase centrosymmetric by compensation. However, if there is any cooperative effect of the individual transverse electric dipoles of the azoxy group, as suggested by Kast[14] in the hypothesis of "swarms", it should be possible to orient these swarms with small d.c. electric fields of a few thousand volts/cm. The nematic phase should become ferroelectric and produce SHG.

We tried SHG in AA using such an arrangement, with an electric field up to 1.5 kV/cm. The axes of the swarms were oriented across the field and the direction of the laser beam, by rubbing the glass surfaces of the cell, according to the Chatelain's technique[15]. Within the accuracy of our measurements, we have not been able to detect any SH signal, using a ruby laser. It may be that some impurities in the sample are responsible for conduction, heat dissipation and turbulence in the nematic mesophase. It is simpler to assume that there is no cooperative effect of the transverse electric dipoles inside the swarms, in agreement with the model of Maier[16] for the dielectric constant of nematic liquid crystals.

In addition to CEC, we tried SHG on the Grandjean texture of some other simpler cholesteric liquid crystals, such as cholesteryl acetate and propionate, without success. In CEC itself we explained SGH by the presence of crystals in the sample. It could be possible, however, that a smectic phase, in CEC, would also give SHG. To test this point, one needs to isolate smectic CEC. We have not been able to do so, and we don't even know if such a smectic phase exists for this compound.

More generally, it is interesting to investigate whether other simpler smectic liquid crystals can generate SH. We have to use materials which are piezoelectric in their crystalline phase, because the symmetry of the mesophase is always higher than the one of the crystal. To test which crystal of a smectic compound lacks a center of inversion, we use SHG as a probe. The experimental setup is shown on Fig. 3(b). A reflection technique[17] is used because of the large light scattering from these crystals and their smectic mesophase. Among many others, we found that three crystals—namely, cholesteryl laurate, nonanoate and decanoate—were piezoelectric. They generate a SH intensity of only a factor 4 below that of a quartz powder, also in reflection.

We then tried to observe SHG from the smectic phase of these compounds. We melt the crystals to the isotropic phase. On slowly cooling, one first observed the colored cholesteric phase, next the smectic one (these materials are monotropic). As long as the samples were in the isotropic, cholesteric or smectic phases, we saw no detectable SH signal. As soon as the samples recrystallized, the SH signal resumed the same intensity as occurred with the initial crystalline powder. This transition was very sharp. The sensitivity of our system allowed the detection of an harmonic signal three orders of magnitude below that of quartz powder.

IV. Conclusion

Contrary to what has been recently claimed,[7] we have not found a single case where SHG of light can be attributed to a mesomorphic mesophase of a liquid crystal. In the reported case of CEC, it is the particular dynamics of melting of ordinary crystals which simulates a phase transition, but we have no evidence of any contribution to

SHG from its mesophase. This result is confirmed by the absence of SHG on other nematic, cholesteric or smectic mesomorphic materials, which do have a piezoelectric crystalline phase.

We can conclude that, in all the cases we studied, the mesomorphic phases of liquid crystals are centrosymmetric, by compensation, as are ordinary liquids. More experiments on other liquid crystals are, of course, necessary to make any definitive statement but we believe that this inversion symmetry is a general property of mesomorphic states. This conclusion agrees with the results of recent X-ray mesomorphic structure determinations[18] where a close packing model has been proposed. The unit cell in the crystal contains an even number of molecules. If the crystal is piezoelectric, it can have, say, C_2 symmetry. In a smectic phase, for example, the long axes of the molecules would not be changed very much, but each molecule would become free to rotate around its C_2 axis. The mean symmetry of the mesophase would thus become C_{2h}, with a center of inversion.

Finally we stress that this inversion symmetry by compensation is valid for mesomorphic domain sizes which are comparable to the wavelength of light, because we used coherent second harmonic generation. Incoherent SHG has also been observed[19] in liquids composed of molecules lacking a center of inversion. In this radiation process each individual molecule acts as an independent source. It would be interesting to observe incoherent SHG from mesomorphic compounds at different temperatures to derive structural information over much shorter distances, of the order of molecular dimensions.

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