# Second harmonic generation in liquid crystals; symmetry of molecules and macroscopic nonlinearity

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Second-harmonic generation was experimentally registered in a nematic liquid crystal in both synchronous and non-synchronouns interactions, and the components of the nonlinear susceptibility tensor were measured for the first time.

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1. We report here confirmed registration of second-harmonic generation (SHG) in oriented samples of the nematic liquid crystal (NLC) MBBA. The different components of the nonlinear susceptibility were obtained experimentally for the first time ever. We measured both the nonsynchronous and synchronous SHG and determined the optimal thickness of the NLC for SHG. The data obtained for different types of interactions can be fully explained by resorting to new assumptions concerning the symmetry and macroscopic properties of NLC.

2. The SHG was obtained in homogeneous cells of MBBA (of chemically-pure grade) of thickness on the order of 10 $\mu$m for the nonsynchronous interaction and of several dozen microns for the synchronous interaction; the orientation was produced in the cells by abrasion of glass substrates in the field of a single-mode $Q$-switched YAlG:$Nd^{3+}$ laser ($\lambda = 1.06\ \mu$m) with radiation power density in the cell on the order of several GW/cm$^2$. The use of a registration system based on a photomultiplier provided a SHG sensitivity limit ($\lambda = 0.53\ \mu$m) at a level of several photoelectrons. For the synchronous SHG it was possible to obtain a 90° temperature synchronism (the accuracy of temperature stabilization in the thermostat was within 0.1 °C).

The angular and spectral widths of the registered signals from the NLC cell (after substracting the background) was typical of SHG. In the experiment we considered the case of collinear SHG, and the components of the tensor $\chi^{(2)}_{ijk}$, measured in this case are shown in Columns II and III of Table I for different types of interactions (Column I). Column IV lists the experimental values components $\chi^{(2)}_{ijk}$ of MBBA, normalized to the value for $\chi^{(2)}_{333}$. Table I shows also the coherent interaction lengths for nonsynchronous SHG at room temperature (Column V). The absolute value for MBBA was obtained from measurements relative to SHG in quartz, and amounts $\chi^{(2)}_{333} = 2 \times 10^{-10}$ cgs esu. Figures 1(a) and 1(b) show the results for synchronous SHG (the possibility of synchronous interaction, both with respect to angle and with respect to temperature for MBBA, is marked by the symbol "+" in Column VI).

In a non-oriented MBBA sample in its isotropic phase, the SHG signal power $P_{2\omega}$ decreased substantially and was at the limit of the sensitivity of the experimental setup.

  

TABLE I.

| I | II | III | IV | V | VI | | VII | VIII |
|---|---|---|---|---|---|---|---|---|
| | | | | | Possibility of synchronism, | | Nonzero components of $\chi_{ijk}^{(2)}$ in the symmetry class "$m$". | |
| Type of interaction | Components of $\hat{\chi}^{(2)}$ for interaction along the $x$ axis | Components of $\hat{\chi}^{(2)}$ for interaction along the $y$ axis, "+" for $\phi = \pi/2$, "−" for $\phi = 3\pi/2$. | Experimental results for $\chi_{\text{norm}}^{(2)} = \chi_{ijk}^{(2)}/\chi_{333}^{(2)}$ | $l_{\text{coh}} = \pi/\Delta k$, $\mu$m. | a) with respect to angle, | b) with respect to temperature | a) For interaction along the $x$ axis | b) For interaction along the $y$ axis, "+" for $\phi = \pi/2$ and "−" for $\phi = 3\pi/2$. |
| $ee-e$ | (333) | (333) | 1 | 0.9 | − | − | (333) | (333) |
| $ee-o$ | (233) | (133) | 0 | 1.6 | + | + | 0 | (133) |
| $oo-e$ | (322) | (311) | 0.05 | 0.5 | − | − | (322) | (311) |
| $oo-o$ | (222) | (111) | 0 | 2.5 | − | − | 0 | (111) |
| $oe-e$ | $\frac{(322)}{2}+\frac{(333)}{2}-(332)$ | $\frac{(311)}{2}+\frac{(333)}{2}\pm(331)$ | 0 | 0.6 | − | − | $\frac{(322)}{2}+\frac{(333)}{2}$ | $\frac{(311)}{2}+\frac{(333)}{2}\pm(331)$ |
| $oe-o$ | $(223)-\frac{(222)}{2}-\frac{(233)}{2}$ | $\frac{(111)}{2}+\frac{(133)}{2}\pm(131)$ | 0.22 | 7.5 | + | + | (223) | $\frac{(111)}{2}+\frac{(133)}{2}\pm(131)$ |

Here $\chi_{ijk}^{(2)}=\chi_{ikj}^{(2)}$



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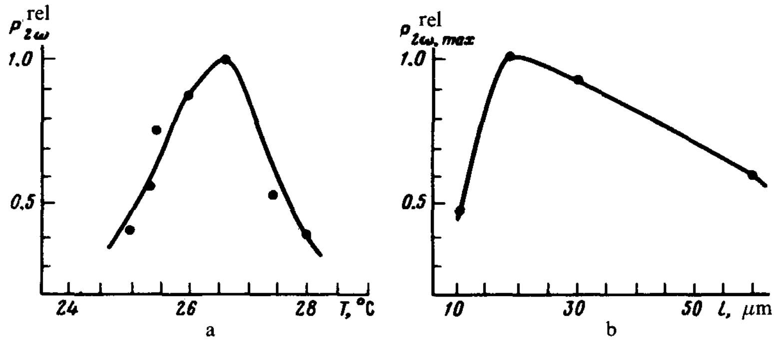


FIG. 1. Plot of temperature synchronism in SHG for a cell of thickness $l = 18$ μm (Fig. a), and dependence of the power $P^{rel}_{2\omega,max}$ at the maximum of the synchronism on the cell thickness (Fig. b) for the *oe–o* interaction in the nematic liquid crystal MBBA.

In the solid phase of the NLC, the value of $P_{2\omega}$ was comparable with the value in the case of synchronous generation in the nematic phase, but no special investigations were made for this case.

3. It follows from the foregoing that the fact that we observed SHG in MBBA in our experiments is subject to no doubt. The value of the registered signal depended substantially on the degree of orientation of the NLC molecules in the cell. Better efficiency should be expected in this case when the NLC molecules are oriented by an external constant magnetic field. In the case of non-oriented NLC, noticable SHG is also possible if the regions of the spontaneous orientation of the molecules are comparable with the wavelength. This must be taken into account in nonlinear interactions of high order in NLC, when an important role can be played by cascade processes. The presence of synchronous generation points to SHG in the bulk of the crystal. With increasing thickness of the NLC layer (or with increasing temperature), when the degree of homogeneous orientation of the molecules becomes worse (influence of the statistics of the medium), the value of $P_{2\omega}$ decreases, and this also explains the relatively small excess of $P_{2\omega}$ in synchronous SHG over the nonsynchronous one, and leads to the presence of an optimal thickness of the cell with the NLC (in our case $l \sim 18$ μm). The low effectiveness of the SHG in our experiments ($\chi^{(2)}_{333} = 2 \times 10^{-10}$ cgs esu) is more readily due not to the general properties of the NLC, but to the fact that so far the investigations were made on "random" NLC, and no task-oriented search for the most effective liquid crystals in nonlinear optics was made. Such materials should be liquid crystals with conjugated chemical bonds, whose molecules have an excited state with intramolecular charge transfer (cf. Ref. 1).

SHG is possible in this experiment on account of the quadrupole electric interaction with nonlinearity of higher order ($P_i^{NL} \chi^{(3)}_{ijkl} E_j \nabla_k E_l$), but such effects should be weak in NLC (in a calcite crystal, for example, in this case the experimental effective susceptibility was estimated at $10^{-18} - 10^{-17}$ cgs esu, Ref. 2).

Thus, SHG should be directly connected with the symmetry of the NLC molecules, many of which can be assigned the symmetry class "*m*"[3-5] (optically biaxial molecules having no inversion center). It should be noted that the experiments aimed at measuring the order parameter in oriented NLC are not very sensitive to biaxiality of the molecules.[6] The values of the components $\chi^{(2)}_{ijk}$ for this class are shown in the components VII–VIII of Table I. The long axis of the NLC molecules corerspond to the $z$ axis, while the $y$ axis is perpendicular to the symmetry plane and it is assumed that in planarly oriented NLC cells the planes of the molecules are perpendicular to the surfaces of the substrates.[4]

A complete explanation of the experimental results on the SHG (see Table I, the last two lines) is possible under additional assumptions. In particular, for interaction along the $x$ axis (see Column II) it must be assumed that the Kleinman symmetry rule[7] is violated for the components $\chi^{(2)}_{ijk}$, in which case $\chi^{(2)}_{332}\neq 0$, a fact that does not correspond to the symmetry class "$m$".

Another explanation is also possible and results in good agreement (within several percent) with the experimentally obtained zero value of the effective susceptibility for the *oe–e* interaction, but which calls for resorting to assumptions that are esentially new for NLC. We have in mind a new electro-magnetooptical effect (high-frequency) due to the action of the polar vector $\mathbf{E}\times\mathbf{H}$ of the light wave (cf. Ref. 8). Such effects can be separated from other orientational interactions in NLC only for experiments in which the polarity of the interaction manifests itself. In this case one measures in the experiments the components that are underlined in Table I. We are unable to dwell here on a discussion of this assumption (see also Ref. 9), but note only that the interaction of the magnetic field of the light wave with the medium is physically realizable: for example it is well known that the magnetic permeability of ferromagnets at optical frequencies is no longer so small—of the order of the magnetic permeability of paramagnets in static magnetic fields.[10] Of great importance in this respect is the concept of the magnetic state of NLC as an analog of ferromagnetic anisotropy.[9]

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