Submitted to Physical Review Letters

UCRL-19623
Preprint

c.2

RECEIVED
LAWRENCE
RADIATION LABORATORY
MAY 27 1970
LIBRARY AND
DOCUMENTS SECTION

PHASE-MATCHED THIRD-HARMONIC GENERATION IN CHOLESTERIC LIQUID CRYSTALS

J. W. Shelton and Y. R. Shen

April 1970

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

UCRL-19623 c.2

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

34

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Phase-Matched Third-Harmonic Generation in Cholesteric Liquid Crystals

J. W. Shelton and Y. R. Shen

Department of Physics, University of California
and
Inorganic Materials Research Division,
Lawrence Radiation Laboratory,
Berkeley, California 94720

ABSTRACT

Using De Vries' model, we predicted theoretically that phase-matching of optical third-harmonic generation can be achieved in cholesteric liquid crystals. The prediction was verified by measurements of third-harmonic generation from a mixture of cholesteryl chloride and cholesteryl myristate.

Phase-matched third-harmonic generation has been observed in crystals[1] and in dye solutions.[2] In crystals, phase-matching was achieved through linear birefringence of the crystal, and in dye solutions, through the anomalous dispersion of the dye. Here, using De Vries' model for cholesteric liquid crystals,[3] we show that phase-matching of third-harmonic generation can also be achieved in a cholesteric liquid crystal through its peculiar properties derived from the helical structure. It has been suggested that phase-matching is possible in an optically active medium through compensation of color dispersion by circular birefringence,[4] but this is not quite the case here. Our prediction has been verified by the experimental results presented later in the paper. So far as we know, this is the first demonstration that phase-matched harmonic generation can be realized in a medium with a position-dependent dielectric constant. The good agreement between theory and experiments has constituted a very strong support of the model of De Vries.[3]

A cholesteric liquid crystal can be visualized as consisting of many thin layers.[5] In each layer, the molecules are all aligned along a certain direction, but in successive layers, the direction of molecular alignment is turned through an angle ϕ. The medium then has an overall helical structure with the helical axis perpendicular to the layers. To explain the linear optical properties of a cholesteric liquid crystal, De Vries[5] used a continuum model. He treated the medium as a birefringent crystal twisted about one of the principal axes into a uniform helical structure with a pitch p. For propagation of infinite plane waves along the helical axis (taken as the z-axis),

the wave equation has the form

$$[(\partial^2/\partial z^2) + \omega^2 \underset{\approx}{\varepsilon}(z)/C^2]\underset{\sim}{E}(z,\omega) = -(4\pi\omega^2/C^2)\underset{\sim}{P}^{NL}(z,\omega) \tag{1}$$

where $\underset{\sim}{E}(z,\omega)$ is the optical field at frequency ω, $\underset{\approx}{\varepsilon}(z)$ is the corresponding dielectric constant varying with z, and $P^{NL}(z,\omega)$ is the nonlinear polarization at frequency ω. This wave equation is most easily solved by first making a rotational transformation $\underset{\approx}{R}(\theta)$, with $\theta=2\pi z/P$, to a twisted coordinate frame. In this twisted coordinate system, Eq. (1) becomes

$$[\frac{\partial^2}{\partial z^2} - (\frac{2\pi}{p})^2 + \frac{4\pi}{p}\underset{\approx}{\sigma}\frac{\partial}{\partial z} + \frac{\omega^2}{C^2}\underset{\approx}{\varepsilon}_T]\,\underset{\sim}{E}_T(z,\omega) = -(\frac{4\pi\omega^2}{C^2})\underset{\sim}{P}_T^{NL}(\omega) \tag{2}$$

where $\underset{\sim}{E}_T=\underset{\approx}{R}\underset{\sim}{E}$, $\underset{\sim}{P}_T^{NL}=\underset{\approx}{R}\underset{\sim}{P}^{NL}$, $\underset{\approx}{\sigma} = R(3\pi/2)$, and $\underset{\approx}{\varepsilon}_T$ is diagonalized with principal values ε_ξ and ε_η along the two principal axes $\hat{\xi}$ and $\hat{\eta}$ in the plane perpendicular to $\hat{z}$.

For the linear case, $\underset{\sim}{P}^{NL}=0$, the solution of Eq. (2) for waves propagating along the $\hat{z}$ direction is[3]

$$\underset{\sim}{E}_T(z,\omega) = \sum_{j=\pm}\begin{pmatrix}\mathcal{E}_\xi\\ \mathcal{E}_\eta\end{pmatrix}_j \exp[im_j(\omega/C)z - i\omega t) \tag{3a}$$

$$|m_\pm^{(\omega)}| = \{(\varepsilon+\lambda'^2) \pm [(\varepsilon+\lambda'^2)^2 - (\varepsilon-\lambda'^2)^2 + \alpha^2]^{1/2}\}^{1/2} \tag{3b}$$

$$(\mathcal{E}_\eta/\mathcal{E}_\xi)_j \equiv if_j = i[m_j^2+\lambda'^2 + (\alpha-\varepsilon)]/2m_j\lambda' \tag{3c}$$

where $\varepsilon=(\varepsilon_\xi+\varepsilon_\eta)/2$, $\lambda'=2\pi C/\omega p$, $\alpha=(\varepsilon_\xi-\varepsilon_\eta)/2$, and m_- is negative for $\lambda'^2 > \varepsilon_\xi$. In the ranges $\alpha < \lambda'^2 << \varepsilon_\eta$ and $\lambda'^2 >> \varepsilon_\xi$, the two modes are nearly left and right circularly polarized respectively.

For third-harmonic generation, $\underset{\sim}{P}_T^{NL}(3\omega)=\underset{\approx}{\chi}_T^{NL}\,\underset{\sim}{E}_T(\omega)\underset{\sim}{E}_T(\omega)\underset{\sim}{E}_T(\omega)$, and the solution of Eq. (2) with the usual parametric approximation is

$$\underset{\sim}{E}_T^{(3\omega)}(z) = \sum_{j,k,\ell,n} A_j (\underset{\approx}{\chi}_T^{NL})_{jk\ell n} \underset{\sim}{\varepsilon}_{Tk}^{(\omega)} \underset{\sim}{\varepsilon}_{T\ell}^{(\omega)} \underset{\sim}{\varepsilon}_{Tn}^{(\omega)} \frac{\sin[\Delta m_{jk\ell n}(\omega z/2C)]}{\Delta m_{jk\ell n}(\omega/2C)}$$

$$\times \exp[i m_j^{(3\omega)}(3\omega z/C) + i\Delta m_{jk\ell n}(\omega z/2C) - i3\omega t] \tag{4}$$

with

$$A_j = i2\pi(3\omega/C)/[m_j^{(3\omega)} - 4\pi C f_j^{(3\omega)}/3\omega p(1+f_j^2)]$$

$$\Delta m_{jk\ell n} = m_k^{(\omega)} + m_\ell^{(\omega)} + m_n^{(\omega)} - 3m_j^{(3\omega)} \tag{5}$$

The third-harmonic generation is most efficient when the phase matching condition $\Delta m_{jk\ell n} = 0$ is satisfied. This is possible in a cholesteric liquid crystal. Given ω, ε, and α, one can find from Eqs. (3b) and (5) a pitch p, which makes $\Delta m_{jk\ell n}=0$, for some combinations of j, k, ℓ, and n. In particular, we can have $\Delta m_{++++}=0$, since in Eq. (3b), ε normally increases with ω, but λ' is inversely proportional to ω. It is interesting to note that in the laboratory frame, each normal mode can be decomposed into two (dependent) circularly polarized propagating modes with refractive indices $n_j^{\mp}(\omega) = [(\omega/C)m_j \pm Q]/(\omega/C)$, and hence $\Delta m_{++++}=0$ leads to $n_+^{\mp}(\omega) - n_+^{\pm}(\omega)=3[n_+^{\pm}(3\omega)-n_+^{\pm}(\omega)]$. The last expression indicates that at phase matching, the color dispersion is compensated through circular birefringence between the two (dependent) propagating modes.

For $\Delta m_{++++} \approx 0$, the third-harmonic intensity is proportional to $|\underset{\sim}{E}^{(3\omega)}(z)|^2$ with $|\underset{\sim}{E}^{(3\omega)}(z)|^2$ given approximately by

$$|\underset{\sim}{E}^{(3\omega)}(z)|^2 = |E_T^{(3\omega)}(z)|^2$$

$$\cong |A_+(\underset{\approx}{\chi}_T^{NL})_{++++}(\underset{\sim}{E}_{T+}^{(\omega)})^3|^2 \frac{\sin^2[\Delta m_{++++}(\omega z/2C)]}{(\Delta m_{++++}\omega/2C)^2} \tag{6}$$

The nonlinear susceptibility $(\chi_T^{NL})_{++++}$ should be non-zero from symmetry arguments if the birefringence factor α is non-zero. Its value can be estimated from absolute intensity measurements of third-harmonic generation at phase-matching.

In our experiments, the cholesteric liquid crystal used is a mixture of 1.75 cholesteryl chloride and 1 cholesteryl myristate.[7] The pitch of this cholesteric liquid crystal can be adjusted from -1.7μ to $\pm\infty$ to $+2\mu$ by varying the temperature from 20°C to 68°C. Using the diffraction method with a He-Ne laser,[8] we measured the pitch as a function of temperature, as shown in Fig. 1. We also measured, using the prism method,[9] the optical dielectric constants at 80°C where the material is in the liquid state. We found $\varepsilon(\omega)=2.19$ and $\varepsilon(3\omega) = 2.30$ with ω corresponding to the 1.06 μ Nd laser frequency. These values were assumed for ε in Eq. (3) over the whole range of temperature. From measurements of optical activity of the sample, we also calculated the birefringence factor α as a function of temperature[3,10] (Fig. 2). This was done at the He-Ne laser frequency (6328 Å) and we assumed that the dispersion of α is negligible. Knowing the values of ε and α, we then predicted from Eqs. (3) and (5) that the phase matching condition, $\Delta m_{++++}=0$, for third-harmonic generation with a Nd laser should occur at $p= -17.3\mu$ and 17.4μ, corresponding to the temperatures 49.4 ± .2°C and 54.2 ± .2°C respectively. Most of the uncertainty in this prediction, we believe, arises from uncertainties in the measurements of p vs T and the color dispersion. Slight change in α does not affect the phase-matched temperature appreciably. Both cholesteryl chloride and cholesteryl myristate are transparent at

the Nd laser frequency and at its third harmonic.

In our experiments of phase-matched third-harmonic generation, we required a nearly homogeneous, single-domain, cholesteric liquid crystal with its helical axis perpendicular to the cell windows. By inducing a shear in the material, we were able to obtain such samples with thickness up to 0.5 mm. In the experiments on third-harmonic generation, we used a sample 130 μ thick. It was immersed in a water bath with the temperature controlled to within ± 0.1°C. A mode-locked Nd:glass laser was used as the fundamental pump field in the third-harmonic generation. The laser was mode-locked so that the total number of third-harmonic photons generated in each shot could be more. Because the sample was thin, the broad spectral width of the laser would not affect the results on generation of third harmonics. The laser beam was normally incident on the sample. In order to have the fundamental waves propagating in the sample to be mainly in the "+" mode, we circularly polarized the laser beam. This also had the advantage of eliminating the background third-harmonic radiation generated from the cell windows, optical filters, and the water bath, since no third-harmonic can be generated in an isotropic medium by a circularly polarized beam.[11] Our experimental arrangement was basically the same as those of others.[12] The third-harmonic signals from the liquid crystal were always normalized against the reference signal of third-harmonics generated from a phase-matched Fuchsin Basic dye cell.[2]

The experimental results of variation of third-harmonic intensity around the phase-matching temperatures are shown in Fig. 3. The two peaks at $p < 0$ ($T < 51.9°C$) and at $p > 0$ ($T > 51.9°C$) correspond

respectively to fundamental pump waves being left and right circularly polarized, as predicted by the theory. The peaks appear at temperatures within 0.1°C of the predicted phase-matching temperatures. The theoretical phase-matching curve is also shown in the figure for comparison with the experimental data. The experimental peaks are definitely broader with no clear fine structure at the wings. This is probably due to the slight variation of the helical pitch in the sample, especially near the boundary surfaces. Since the molecular structures for $p < 0$ and for $p > 0$ are different and χ^{NL}_{++++} could vary accordingly, we would not expect the two phase-matching peaks to be of the same height. Experimentally, we found that the two peaks were different in height, but their difference was within the 20% experimental accuracy.

The third-harmonic output was found to be elliptically polarized with the ratio of the two circularly polarized components being 5 ± 1. The theoretical ratio, given by[3] $|[(\lambda'-\varepsilon\frac{1}{2})f_+^{(3\omega)}-m_+^{(3\omega)}]/[(\lambda'+\varepsilon\frac{1}{2})f_+^{(3\omega)}-m_+^{(3\omega)}]|^2$ is 4.8. Comparison of the phase-matched third-harmonic signals from the liquid crystal and from the Fuchsin Basic dye solution yields $|\chi^{NL}_{++++}|/|\chi^{NL}_{Dye}| \approx 0.1$. We also measured the phase-matched third-harmonic generation from samples with different thickness. The third-harmonic intensities were indeed roughly proportional to the square of the sample thickness. Investigation of phase-matching conditions $\Delta m_{jk\ell n}=0$ with other combinations of $jk\ell n$ is presently in progress.

In summary, we have shown that the third-harmonic generation in a cholesteric liquid crystal is phase-matchable. This effect should be common for nearly all cholesteric liquid crystals. That our experimental

results agree well with the theory is another triumph of De Vries' model[3] for cholesteric liquid crystals.

ACKNOWLEDGEMENTS

We would like to thank Dr. N. M. Amer for helpful discussions.

This work was performed under the auspices of the U. S. Atomic Energy Commission.

REFERENCES

1. P. D. Maker and R. W. Terhune, Phys. Rev. 137, A801 (1965).
2. P. P. Bey, J. F. Giuliani, and H. Rabin, Phys. Rev. Letters 19, 819 (1967).
3. H. N. De Vries, Acta. Cryst. 4, 219 (1951).
4. H. Rabin and P. P. Bey, Phys. Rev. 156, 1010 (1967).
5. G. W. Gray, Molecular Structure and the Properties of Liquid Crystals, (Academic Press, N.Y., 1962) p. 39.
6. See, for example, A. Yariv, Quantum Electronics (John Wiley, Inc., N.Y., 1967). We have assumed here that two normal propagating modes are orthogonal. In reality, the two modes are not orthogonal, but the effect of non-orthogonality on phased-matched harmonic generation is negligible.
7. Cholesteryl chloride and cholesteryl myristate were obtained from Aldrich Chemical Co. and Eastman Organic Chemicals, Inc. respectively. No further refinement on the materials was done. Impurities may affect the properties of the cholesteric mixture and hence also the phase-matched temperature.
8. E. Sackmann, S. Meiboom, and L. C. Snyder, J. Am. Chem. Soc. 90, 3567 (1968).
9. See, for example, F. W. Sears, Optics (Addison-Wesley Press, Inc., 1949) p. 47.
10. C. Robinson and J. C. Ward, Nature 180, 1183 (1957).
11. H. J. Simon and N. Bloembergen, Phys. Rev. 171, 1104 (1968).
12. R. K. Chang and L. K. Galbraith, Phys. Rev. 171, 993 (1968).

FIGURE CAPTIONS

Fig. 1. Variation of the inverse pitch (1/p) with temperature for the mixture of 1.75 cholesteryl chloride and 1 cholesteryl myristate. The experimental uncertainty is ± 0.005 μ^{-1}. The solid line is an approximate fit to the experimental points.

Fig. 2. Variation of the birefringence factor α as a function of temperature at the He-Ne laser wavelength, 6328 Å, for the mixture of 1.75 cholesteryl chloride and 1 cholesteryl myristate. The solid line is an approximate fit to the experimental points.

Fig. 3. Normalized third-harmonic intensity vs temperature near the phase matching temperatures for the mixture of 1.75 cholesteryl chloride and 1 cholesteryl myristate, in a cell 130μ thick. The peak at the lower temperature (corresponding to left helical structure) is generated by left circularly polarized fundamental waves and the one at the higher temperature by right circularly polarized funamental waves. The solid line is the theoretical phase-matching curve and the dots are experimental data points. The uncertainty in the experimental third harmonic intensity is about 20%.

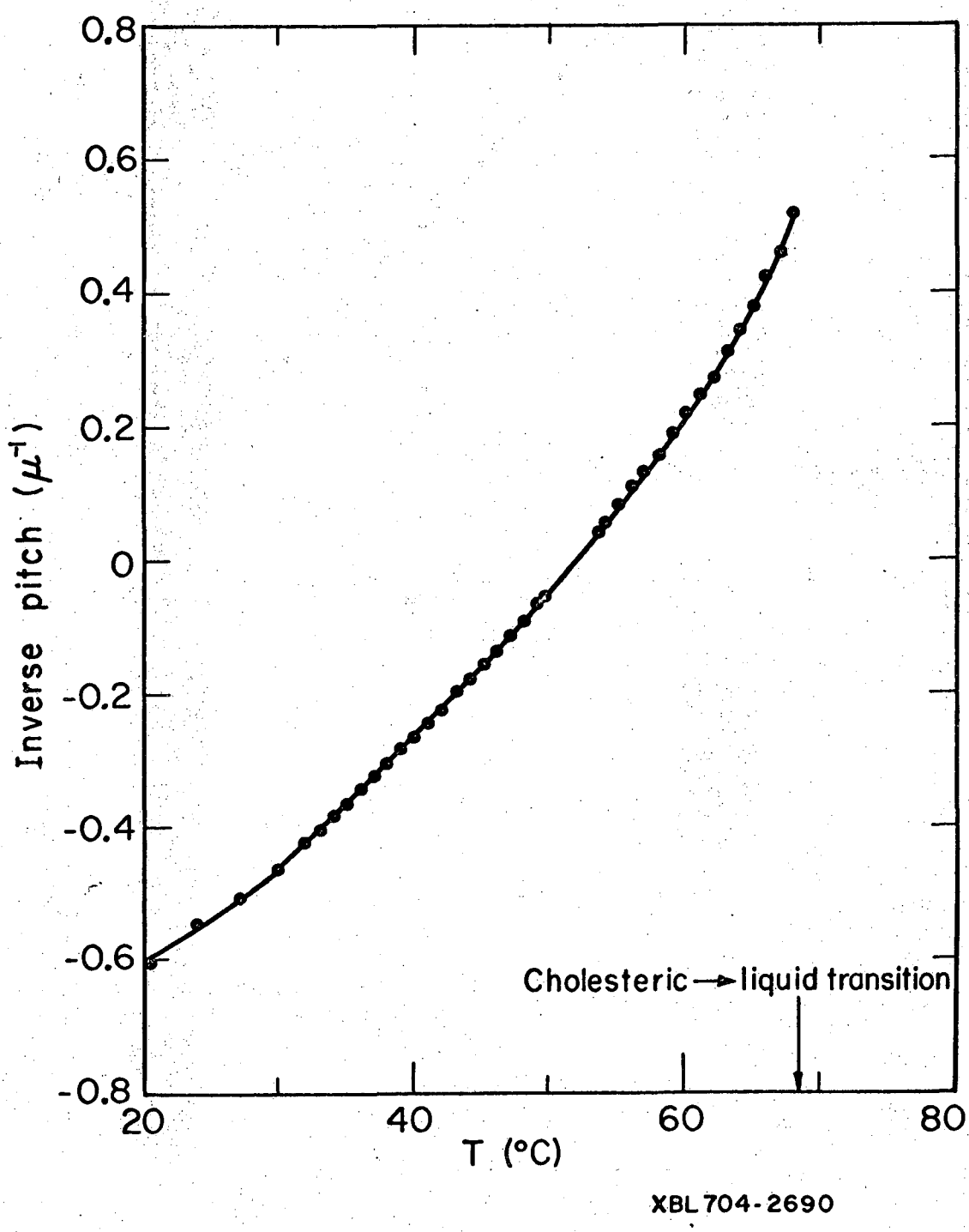

0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
Inverse pitch (μ^{-1})
20
40
60
80
T (°C)
Cholesteric → liquid transition
XBL 704-2690

Fig. 1

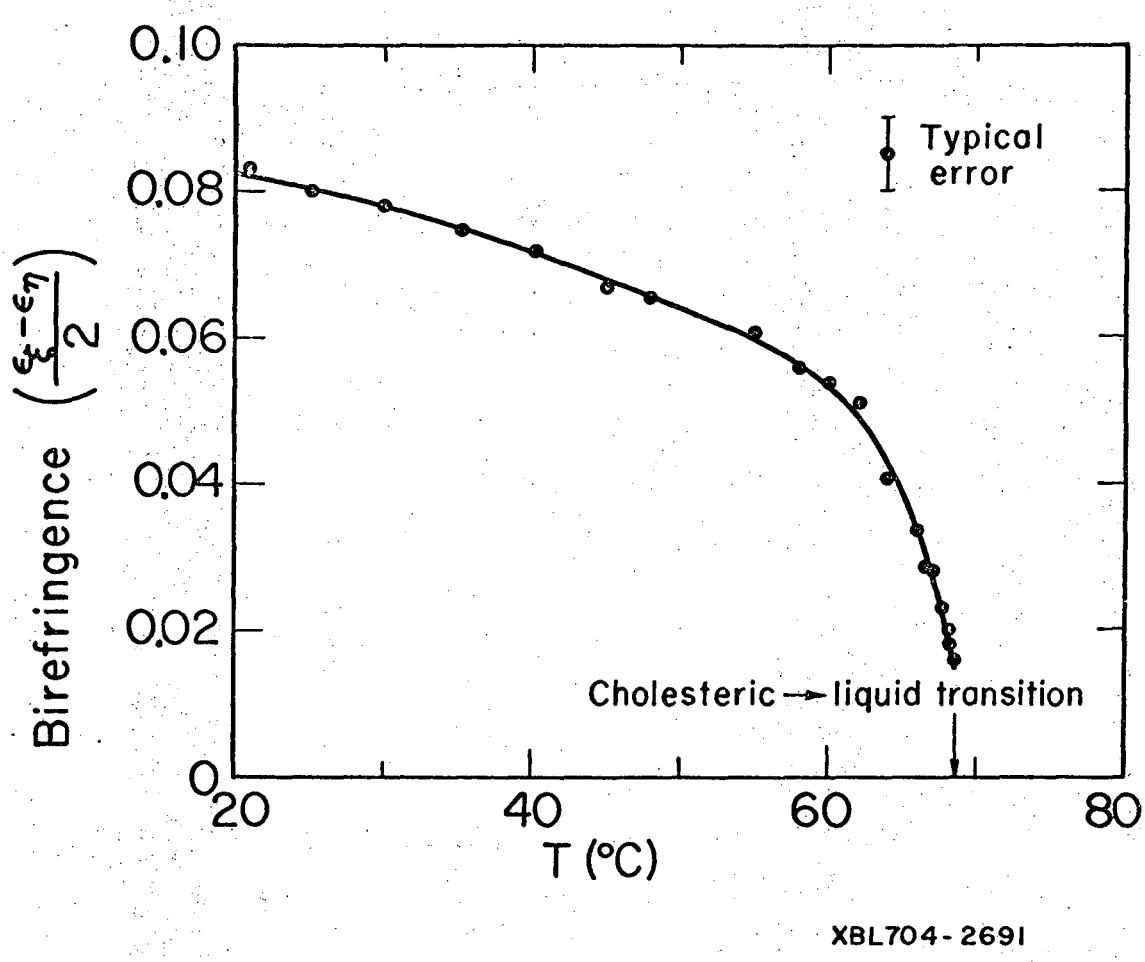
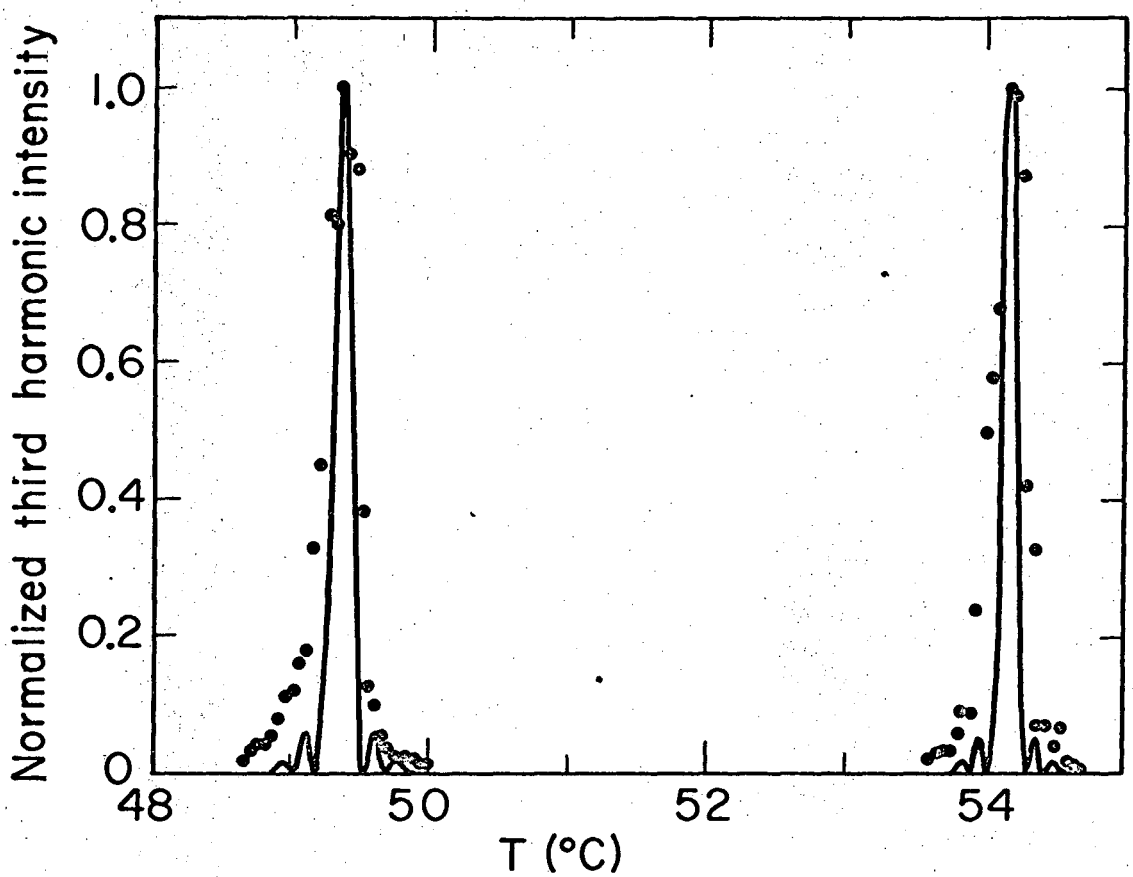

0.10
0.08
0.06
0.04
0.02
0
Birefringence $\left(\frac{\epsilon_\xi - \epsilon_\eta}{2}\right)$
20
40
60
80
T (°C)
Typical error
Cholesteric → liquid transition
XBL704-2691

Fig. 2



XBL 704-2692

Fig. 3

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720