ARCHIVES OF ACOUSTICS
17, 1, 43–50 (1992)

ACOUSTIC RELAXATION NEAR THE ISOTROPIC LIQUID-NEMATIC PHASE TRANSITION IN THE NEMATIC PHASE IN p-n-OCTYLOXY p'CYANOBIPHENYL

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The paper presents the results of the completation measurements on p-n-octyloxy p'cyanobiphenyl [1] of the absorption and the ultrasonic velocity in the smectic-nematic phase for a frequency range varying from. 2.5 MHz to 60 MHz.

In the nematic phase near the isotropic liquid-nematic transition, the contributions to the quantities $\alpha\lambda$ and α/f^2 the critical slowing down of the order parameter, the fluctuations of the order parameter and the director fluctuations were analyzed. Each ultrasonic absorption mechanism was characterized by an appropriate relaxation time near the phase transition.

1. Introduction

The classical theories [2, 3] fail to explain ultrasonic absorption in liquid crystals. The disagreements observed can be explained with the aid of the relaxation theory of absorption which takes into account both the molecular relaxation and the critical molecular relaxation associated with present phase transitions. Near the phase transition temperature, an increase of absorption (decrease of velocity) is observed. However, during the phase transition the maximum of absorption and minimum (or strong change) are observed. Now it has generally been agreed that the interaction of ultrasonic with the order parameter fluctuation [2, 3, 4, 5] is the main mechanism of absorption in the isotropic liquid crystal.

Near the phase transition in the nematic phase three [3, 4] absorption processes are present:

1. Coupling of the sound wave and director fluctuations.
2. Coupling of the sound wave and order parameter fluctuations,
3. Coupling of the sound wave and critical slowing down of the order parameter.

The absorption coefficient

$$\alpha = \alpha_n + \alpha_{\delta s} + \alpha_s + \alpha_v \tag{1}$$

is given by components associated with the appropriate absorption mechanism where: α_n – described the director fluctuations, $\alpha_{\delta s}$ – describes the order parameter fluctuations, α_s – described the slowing down of the order parameter, α_v – described the absorption which is not related to any relaxation process.

According to the results of NAGAI [4], we obtained the following forms for the absorption coefficients referred to the wave length:

$$\alpha_n \lambda(f) = D\frac{f}{f_0}\left\{1 - \frac{f}{4\sqrt{2}f_0}\left(\ln\left|\frac{1+\sqrt{\frac{2f}{f_0}}+\frac{f}{f_0}}{1-\sqrt{\frac{2f}{f_0}}+\frac{f}{f_0}}\right| + 2\,\mathrm{arctg}\,\frac{\sqrt{2ff_0}}{f-f_0}\right)\right\} \tag{2}$$

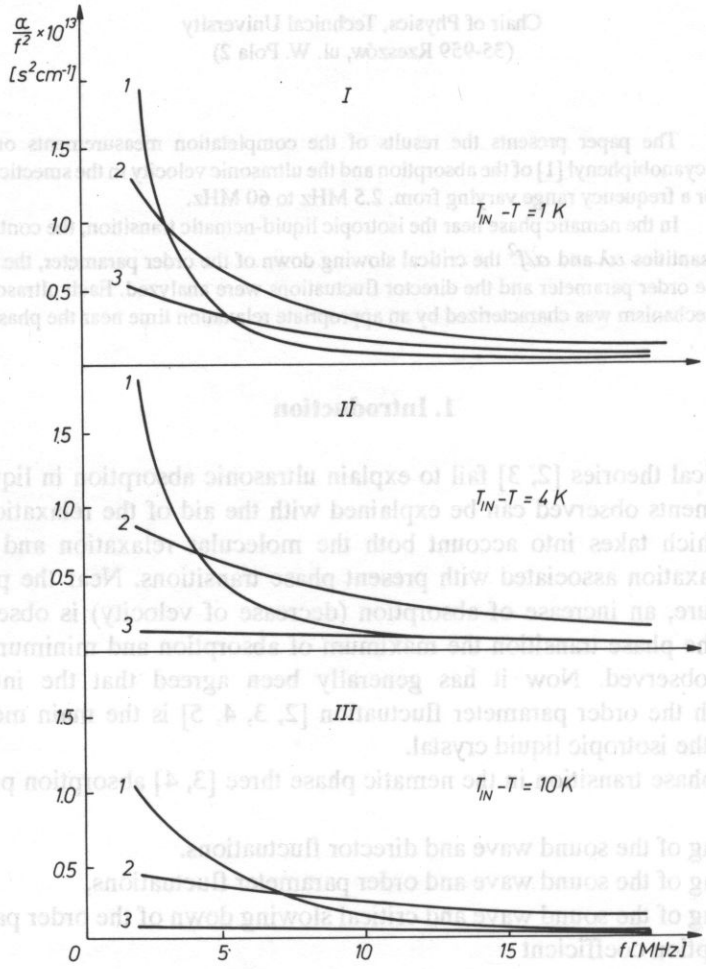

FIG. 1. Contribution of different absorption mechanism in α/f^2 for the mesomorphic nematic phase [5].

$$\alpha_{\delta s}\,\lambda(f) = E\sqrt{\frac{1}{f}}\left(\sqrt{\frac{f_0'}{f}+\sqrt{\left(\frac{f_0'}{f}\right)^2+1}}-\sqrt{\frac{2f_0'}{f}}\right), \tag{3}$$

$$\alpha_s\lambda(f) = F\frac{\frac{f}{f_R}}{1+\left(\frac{f}{f_R}\right)^2}, \tag{4}$$

$$\alpha_v\lambda(f) = Qf, \tag{5}$$

where f_0, f_0', f_R are the relaxation frequencies of the director fluctuation, the order parameter fluctuation and the critical slowing down of the order parameter, respectively. All D, E, F and Q are free parameters which require to be adjusted. MANDELSTAMM and LEONTOWICH [6] explained the observed "above Stokes" part of absorption in terms of losses induced by the volume viscosity. It appears during the volume change in space where the substance is condensed. Starting from the theoretical results [5] obtained for the ultrasonic absorption in the nematic liquid crystals phase near the isotropic liquid-nematic transition, we can write [4, 7, 8]:

$$\frac{\alpha}{f^2} = \frac{2\Pi^2}{\rho V^3}\left(\eta_v^{(s)}(f)+\eta_v^{(\delta s)}(f)+\eta_v^{(n)}(f)\right)+G\alpha_4, \tag{6}$$

where: ρ – liquid crystal density, V – ultrasonic velocity, $\eta_v^{(s)}$, $\eta_v^{(\delta s)}$, $\eta_v^{(n)}$ denote the contribution of the critical slowing down of the order parameter, the order parameter fluctuating and the director fluctuations in volume viscosity, respectively. $G\alpha_4$ denotes the regulator part of the absorption [9]. The components of volume viscosity related to given processes assisting in the critical ultrasonic absorption are given by

$$\eta_v^{(a)}(f) = \frac{A}{1+\left(\frac{f}{f_R}\right)^2}, \tag{7}$$

$$\eta_v^{(\delta s)}(f) = \frac{B}{\sqrt{(2\pi f)^3}}\left[\sqrt{\sqrt{\left(\frac{2f_0'}{f}\right)^2+1}+\frac{2f_0'}{f}}-\sqrt{\left(\frac{4f_0'}{f}\right)}\right], \tag{8}$$

$$\eta_v^{(n)}(f) = \frac{C}{2\pi f_0}\left\{1-\frac{1}{2}\sqrt{\frac{f}{2f_0}}\left[\frac{1}{2}\ln\frac{\frac{f}{f_0}+\sqrt{\frac{2f}{f_0}}+1}{\frac{f}{f_0}-\sqrt{\frac{2f}{f_0}}+1}+\right.\right.$$

$$\left.\left.+\operatorname{arctg}\left(\sqrt{\frac{2f_0}{f}}+1\right)+\operatorname{arctg}\left(\sqrt{\frac{2f_0}{f}}-1\right)\right]\right\}. \tag{9}$$

Here A, B, C, G are constants which can be calculated from numerical calculations under the experimental results of α/f^2. Starting from the measured quantities $\alpha\lambda$ and α/f^2, one should determine the concentration of particular mechanisms near the phase transition so as to fit the experimental curves to the theoretical ones given by Eqs. (2)–(6). The dependence of different absorption mechanisms on the quantity α/f^2 in the mesomorphic nematic phase is plotted in Fig. 1 [5].

2. Experiment and examined material

The p-n-octyloxy-p′-cyanobiphenyl $C_8H_{17}O-<\overline{O}>-<\overline{O}>-CN$ liquid crystal processes the smectic mesophase and the nematic phase. The temperatures of the phase transitions were determined under the behaviour of the absorption and the velocity during the cooling process (Fig. 2) and the value of enthalpy by the DSC method at the M. Luther University Halle. The obtained results are solid state $\frac{326.35\ \mathrm{K}}{29.3\ \mathrm{KJ/mol}}$ smectic A $\frac{341.45\ \mathrm{K}}{62.5\ \mathrm{J/mol}}$ nematic $\frac{348.55\ \mathrm{K}}{754\ \mathrm{J/mol}}$ isotropic liquid.

The ultrasonic set US-6 (made at the IFTR in Warsaw) was used for absorption measurements which make possible research of liquid crystals (in the frequency range (9.8–60) MHz [10] or in a modified version in the frequency range: (2.5–7.5) MHz.

3. Experimental results, calculations and discussion

The experimental results of the wave propagation velocity for p-n-octyloxy p′-cyanobiphenyl [1] and calculations of $\alpha\lambda$ for five temperatures near the isotropic liquid-nematic transition (this temperature range contains the mesomorphic nematic phase) and formulas (2)–(4) allow us to find the characteristic relaxation frequencies for appropriate mechanisms for a given frequency range. The description of the main absorption processes near the phase transition formulas (1)–(5) requires the need to fit the set of parameters f_0, D, f_0', E, f_R, F and Q for the appropriate. The χ^2 test was used to estimate the quality of fitting with χ^2given by

$$\chi^2 = \sum_f \chi^2(f) = \sum_f \left(\frac{\alpha\lambda_{\mathrm{exp}}^{(f)} - \alpha\lambda_{\mathrm{th}}^{(f)}}{\Delta\alpha\lambda(f)} \right)^2 ,$$

Here $\alpha\lambda_{exp}^{(f)}$ and $\alpha\lambda_{th}^{(f)}$ describe the experimental and theoretical values of the absorption coefficient referred to the wavelength respectively. The experimental error to $\alpha\lambda_{exp}^{(f)}$ described $\Delta[\alpha\lambda_{exp}^{(f)}]$. The parameters were determined from the minimum condition for χ^2. The values of the absorption components associated with particular

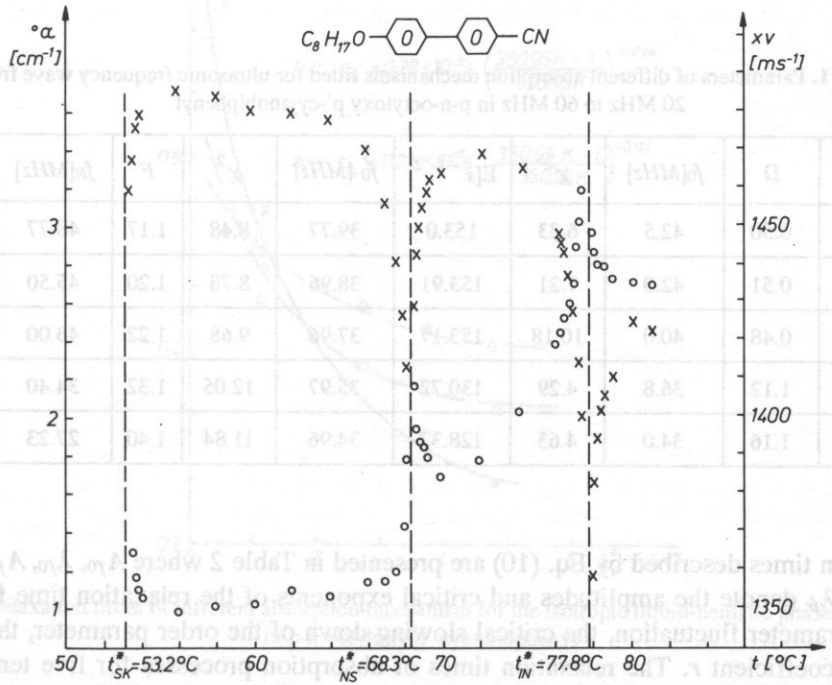

FIG. 2. Absorption and velocity of ultrasonic wave for a frequency equal to 2.5 MHz in p-n-octyloxy p'-cyanobiphenyl.

mechanisms were calculated with the help of the results presented in [4] and [5] (for a frequency range of the ultrasonic wave from 20 MHz to 60 MHz). The estimated parameters describing the absorption referred to the wave length for particular cases are presented in Table 1. Let T_{IN}^* express the temperature for the $N-I$ phase transition which is the minimal temperature for the (metastable) isotropic phase ($T_{IN}^* < T_{IN}$) to exist and is very close to T_{IN} the so-called hypothetical second kind phase transition temperature [11, 12]. Next, the behaviour of the relaxation times ($\tau_{rel} = 1/2\pi f_{rel}$) for absorption mechanisms are described by the Fisher function [13]:

$$\tau = A\left(\frac{T_{IN}^* - T}{T_{IN}^*}\right)^{\lambda}. \tag{10}$$

Here λ is the critical exponent, the amplitude A is constant and T is the absolute temperature. The temperature T_{IN}^{*} and T_{IN} satisfy the inequality $|T_{IN} - T_{IN}^{*}| \leq 1$ K. The critical exponents were determined by least square analysis. The correlation coefficients r was obtained and was in agreement with the Keller criterion [15] with its limit values $|r|$ depending on the measurements data number. The obtained values of the

Table 1. Parameters of different absorption mechanisms fitted for ultrasonic frequency wave from 20 MHz to 60 MHz in p-n-octyloxy p'-cyjanobiphenyl

$T[K]$	D	$f_0[MHz]$	χ^2	$E[s^{-1/2}]$	f_0' [MHz]	χ^2	F	$f_R[MHz]$	χ^2
346.15	0.50	42.5	6.33	153.0	39.77	8.48	1.17	48.77	0.31
347.15	0.51	42.0	7.21	153.91	38.96	8.78	1.20	45.50	0.56
348.15	0.48	40.0	10.18	153.17	37.96	9.68	1.22	43.00	0.65
349.75	1.12	36.8	4.29	130.72	35.97	12.05	1.32	34.40	3.43
350.35	1.16	34.0	4.63	128.37	34.96	11.84	1.40	27.23	9.36

relaxation times described by Eq. (10) are presented in Table 2 where A_{f0}, λ_{f0}, $A_{f'0}$, $\lambda_{f'0}$ and A_{fr}, λ_{fr} denote the amplitudes and critical exponents of the relaxation time for the order parameter fluctuation, the critical slowing down of the order parameter, the correlation coefficient r. The relaxation times of absorption processes for five temperatures are shown in Fig. 3.

We analyzed the variation of α and v with temperature for the constant value of the ultrasonic incidence frequency (Fig. 3). The results indicate that we are dealing with a

Table 2. Quantities of p-n-octyloxy p'-cyjanobiphenyl describing the relaxation times for different absorption mechanisms

$T_{IN}^{*}[K]$	$A_{f0} \cdot 10^{-8}[s]$	λ_{f0}	r
350.95	0.23	-0.113 ± 0.002	0.991
$T_{IN}^{*}[K]$	$A_{f0}' \cdot 10^{-8}[s]$	λ_{f0}'	r
350.95	0.28	-0.086 ± 0.003	0.994
$T_{IN}^{*}[K]$	$A_{fR} \cdot 10^{-8}[s]$	λ_{fR}	r
350.95	0.12	-0.234 ± 0.004	0.995

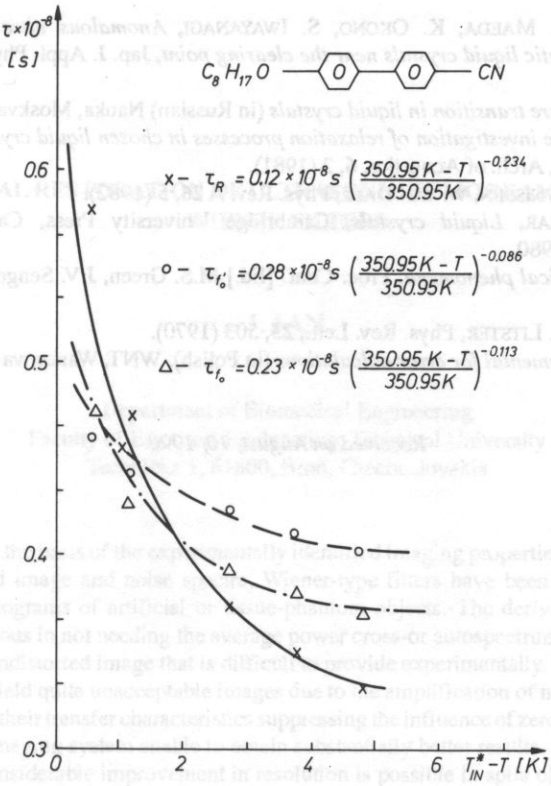

FIG. 3. Relaxation times of different absorption mechanism for the isotropic liquid-nematic phase transition in p-n-octyloxy p'-cyanobiphenyl

relaxation process which is conditioned by the character of the phase transition. The calculated characteristic relaxation times for the critical slowing down of the order parameter and the director fluctuation mechanisms are characteristic qualities near the phase transition.

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Received on August, 10, 1990