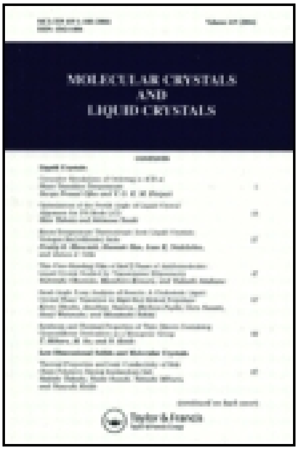

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Determination of the Frank Elastic Constant Ratios in Nematic Liquid Crystals (nCB) by Observing Angular Dependence of Rayleigh Light Scattering Intensity

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Determination of the Frank Elastic Constant Ratios in Nematic Liquid Crystals (nCB) by Observing Angular Dependence of Rayleigh Light Scattering Intensity

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The Frank elastic constant ratios, K_{12} and K_{32}, in a homologous series of *n*CB ($n = 5 - 8$) were determined as a function of temperature by observing the angular dependence of Rayleigh light scattering intensity. The temperature dependence of K_{32} exhibits an odd-even effect. Both K_{12} and K_{32} obtained are clearly smaller than the reported values by means of other methods, e.g., the Frederiks transition method. However, our K_{31} indirectly deduced from K_{32}/K_{12} shows good agreement with that by others. Characteristic temperature dependences due to the appearance of the pretransitional ordering were observed in 8CB which has the smectic A phase below the nematic phase; K_{32} significantly diverges and K_{12} shows a sudden descent as a smectic A is approached. On the basis of these experimental results, we claim that the Rayleigh light scattering is the most adequate method of determining the Frank constant ratios.

1. INTRODUCTION

Three Frank elastic constants, K_{11}, K_{22} and K_{33}, of nematic liquid crystals play an important role in characterizing liquid crystal displays. Especially the ratio of bend to splay elastic constants, $K_{31} = K_{33}/K_{11}$, is desired to be as small as possible for high duty liquid crystal displays.[1] Hence the collection of the accurate ratios by means of a simple method has attracted a keen attention in these days. Among several methods of measuring these quantities, we have been interested in a Rayleigh light scattering technique that requires no large deformation in the director field unlike the Frederiks transition method. Attempts using this method on some nematic liquid crystals have already been reported,[2,3] but, as far as we know, the systematic investigations are scarce up to now. In this paper, we present the results thus obtained and show that the light scattering technique will become a conventional method of determining the Frank elastic constant ratios.

Nematics strongly scatter light and are thus turbid because of the spontaneous fluctuation of the alignment in a nematic medium.[4] When we describe scattering geometries, the important parameters are the wave vectors k_i and k_f of the incident and scattered light inside the sample together with the corresponding polarizations defined by the unit vectors i and f, respectively. The difference $q = k_i - k_f$ is the scattering vector. According to de Gennes,[4] the differential scattering cross section per unit scattering volume is given by

$$\frac{d\sigma}{d\Omega} = \left(\frac{\pi\epsilon_a}{\lambda^2}\right)^2 k_B T \sum_{\alpha=1}^{2} \frac{(i_\alpha f_z + i_z f_\alpha)^2}{\left(K_{33}q_\parallel^2 + K_{\alpha\alpha}q_\perp^2\right)}, \tag{1}$$

where the z axis is taken as the optical axis along the average director orientation. Here $\epsilon_a = \epsilon_\parallel - \epsilon_\perp$ is the anisotropy of the dielectric constant, λ the wavelength of the light used, k_B the Boltzmann constant, and T the absolute temperature.

If we choose $i \perp f$, Eq. (1) is reduced to simple formulae as a function of the scattering angle α between k_i and k_f.[2] The equations contain two parameters K_{12} or K_{32} and $n_{eo} = \sqrt{\epsilon_\parallel} / \sqrt{\epsilon_\perp}$ for a suitable choice of particular geometries, where k_i is always normal to the z axis. Since n_{eo} can be measured independently, we can determine the parameter K_{12} or K_{32} by a fitting procedure between the experimentally obtained angular dependence and the theoretical one calculated from those formulae.

Following the procedure described above, we determined K_{12} and K_{32} of nCB ($n = 5 - 8$) as a function of temperature and compared with those by other methods. In what follows, we will show the experimental details and the results obtained.

2. EXPERIMENTAL

Nematic liquid crystals used were a homologous series of 4'-alkyl-4-cyanobiphenyls (nCB, $n = 5 - 8$) obtained directly from their sealed containers (BDH Chemicals Ltd.) and their transition temperatures agree well with those accepted for these products.[5] Thus any further purification was not attempted. The key to perform a successful experiment is preparing good monodomain cells of reasonable size since the light scattering are extremely sensitive to defects such as dust and disclinations in samples. Therefore the sample preparation was made with great care. Scattering cells consist of two plane parallel microscope slide glass plates, 19 mm × 13 mm × 1.3 mm. The glass plates were sonicated in refined deionized water. To obtain homogeneous alignment, the plates were treated with 0.1 wt% aqueous solution of polyvinyl alcohol and rubbed unidirectionally back and forth several times with turning velvet. Since it was confirmed that the elastic constant ratios determined did not depend on the cell thickness at least between 9 μm and 25 μm, 12μm or 18 μm spacers (Toray Industries, Inc.) were used. By capillary suction, *n*CB was introduced into a cell.

Prior to the scattering measurements, the refractive indices were measured as a function of temperature. The measurements were performed by means of total reflection method[6] with use of a pair of half-cylindrical glasses of high refractive index, $n = 1.8729$. The accuracy of the refractive indices of liquid crystals were ± 0.001, which gave uncertainty of about $\pm 1\%$ in the Frank constant ratios.

A block diagram of our photoelectron counting system for measuring the angular dependence of the scattered intensity is illustrated in Fig. 1. The light source used was an Ar ion laser ($\lambda = 514.5$ nm, Spectra Physics Model-165). The incident laser impinged on a sample cell mounted in a copper oven after passing through a quarter-wave plate, polarizers and pinholes. The scattered beam was detected by a

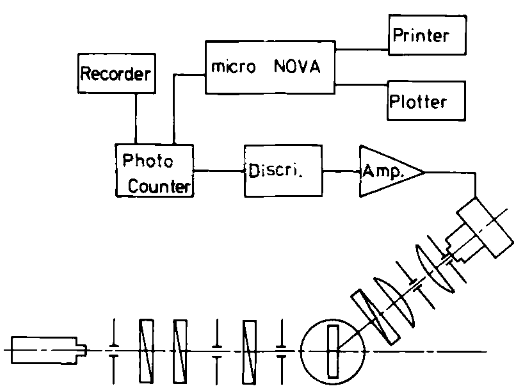

FIGURE 1 Block diagram of our experimental setup.

photomultiplier tube (PMT) for photon counting (Hamamatsu-R649) with a discriminator (Hamamatsu-C1050) through an analyzer, lenses and pinholes used to define the scattering wave vector k_f and the effective scattering volume Ω. They were set on an arm of goniometer. The arm was rotated over the scattering angle measured in air from 5° to 25° in 10 minutes. The number of photons counted in every one second was stored in a minicomputer (micro-NOVA MP/200). The incident light and scattered light intensities were monitored by a chart recorder. The fitting procedure to the theoretical angular dependence was carried out by the minicomputer and the result was printed out by a printer (EPSON MP-80) and a plotter (HP-7225A). The typical deviation from the theoretical calculation was 1 or 2×10^{-2}. Usually it takes about 15 minutes to get one elastic constant ratio at a particular temperature.

The measurements were carried out for two combinations of polarizers; i and f were extraordinary and ordinary polarized light (EO) and vice versa (OE). Both the measurements should give an identical elastic constant ratios if a truely planar cell was used. The two measurements in the EO and OE configurations were able to determine whether the molecules were slightly tilted from the glass surfaces or not. The data obtained using cells with slight tilt were not included in the final results.

3. RESULTS AND DISCUSSION

The experimental results of K_{12}, K_{32} and K_{31} are plotted as a function of the relative temperature, $T_{NI} - T$, in Figs. 2, 3, and 4. In the figures, K_{31}'s are those indirectly deduced from K_{32}/K_{12}, while K_{32}'s and K_{12}'s are the direct results in the present work. The overall profiles show rather gentle increases with increasing $T_{NI} - T$ except near the smectic-nematic transition, T_{AN}, in 8CB. As characteristic features, the following three points will be discussed one by one;

1. Dependence of K_{12} and K_{32} on alkyl chain length,
2. Comparison between our results and others,
3. Characteristic behavior in 8CB as the smectic A phase is approached.

As the first point, the odd-even effect is clearly seen in the temperature dependence of K_{32}, while K_{12} becomes larger with increasing the alkyl chain length. This feature could be quite useful for designing materials for better display devices. The temperature dependence

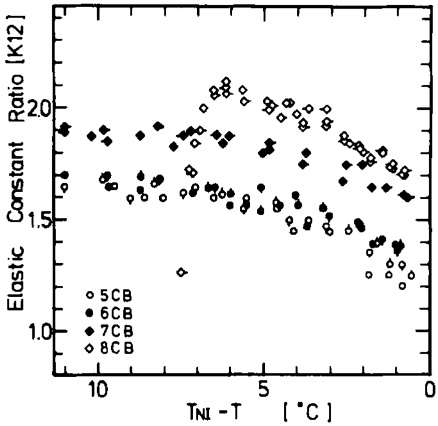

FIGURE 2 Temperature dependence of Frank elastic constant ratio K_{12} in nCB ($n = 5-8$). Results from three different samples are distinguished by different symbols.

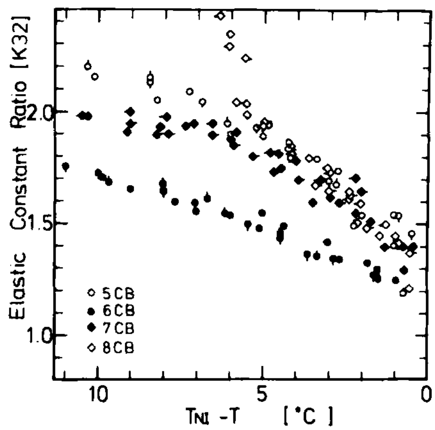

FIGURE 3 The same as Fig. 2 for K_{32}.

behavior in mixed compounds of several nCB is of further interest, since mixed compounds are important in industrial use.

Let us now compare the present results with those by other methods. In Figs. 5, 6, and 7, results in 5CB so far obtained are collected. They were obtained by an optical detection[7-9] or capacitance detection[10] of the Frederiks transition, a shear flow method[11] and optical transmission method.[12] The present results are redrawn by smooth curves. There exists systematic difference between these; our K_{12} and K_{32} values are much smaller than the others as shown in Figs. 5 and

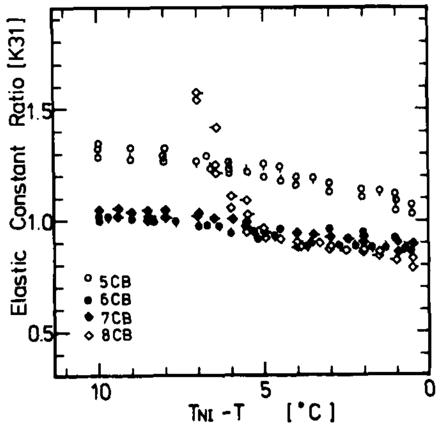

FIGURE 4 The same as Fig. 2 for K_{31}, which is indirectly deduced from K_{32}/K_{12}.

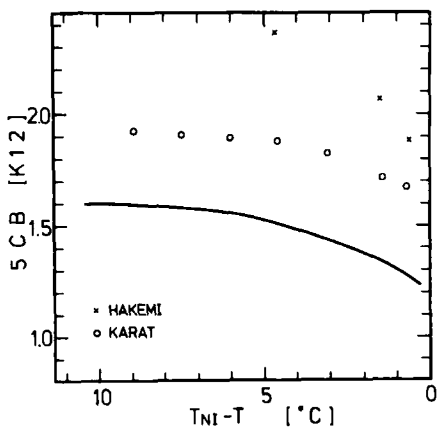

FIGURE 5 Comparison between the present results (smooth curve) and those by other methods for K_{12} in 5CB.

6. It is interesting, however, our K_{31} indirectly deduced from K_{32}/K_{12} shows good agreement with the others as shown in Fig. 7. It is known that the accurate determination of the twist elastic constant K_{22} is difficult in the Frederiks transition method.[7-10] This may be the reason why the collected data of K_{12} and K_{32} widely scatter and are significantly larger than ours, while those of K_{31} agree quite well including ours. Since the present Rayleigh light scattering technique needs no external field, we claim that the light scattering technique will become a simple conventional method of accurately determining the Frank elastic constant ratios.

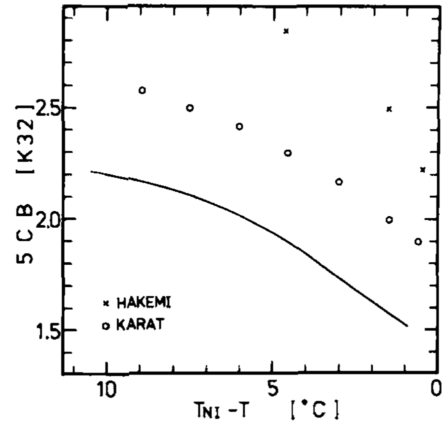

FIGURE 6 The same as Fig. 5 for K_{32}.

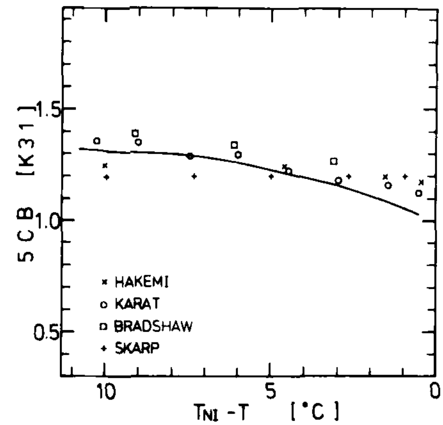

FIGURE 7 The same as Fig. 5 for K_{31}.

Now we turn to the characteristic temperature dependences in 8CB shown in Figs. 2 and 3; K_{32} significantly diverges and K_{12} shows a sudden descent as a smectic A phase is approached. According to the continuum theory, both twist and bend deformation becomes forbidden in an ideal monodomain smectic A with parallel and equidistant layers,[4] resulting in the sudden descent in K_{12} as observed. The divergence of K_{32} shows that the divergence of K_{33} is dominant than that of K_{22}.

The experimental observations of such pretransitional anomalies in the Frank constants have been made by several groups either through

Frederiks transition[13-16] through light scattering.[17] The anomalies have been discussed on the basis of the formation of cybotactic groups of a smectic phase in a nematic phase. But the well defined temperature dependence has not been experimentally established, though the results were described by $(T - T_{AN})^{-x}$.[13-17] This will be one of our future problems.

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