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POLARIZED RAMAN SCATTERING
AND ITS ELECTRIC FIELD EFFECTS IN DOBAMBC

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Résumé. — On observe la diffusion Raman polarisée dans les phases smectique A et smectique C* du (S)-2-méthylbutyl-p-(p-décyloxybenzylidène)-amino-cinnamate, qui est un cristal liquide ferroélectrique. Les rapports de polarisation de l’intensité Raman dépendent fortement de la température dans la phase S_c, mais très peu dans la phase S_A. Cette dépendance en température est expliquée par les variations de l’angle d’inclinaison de l’axe moléculaire. Sous champ électrique, on constate une variation anormale avec la température du rapport de polarisation à la transition S_A-S_C.

Abstract. — Polarized Raman scattering is observed in aligned smectic A and smectic C* phases in (S)-2-methylbutyl-p-(p-decyloxybenzylidene)-amino-cinnamate, which is known as a ferroelectric liquid crystal. The polarization ratios of the Raman intensity strongly depend on temperature in the smectic C* phase but scarcely in the smectic A phase. This temperature dependence is qualitatively explained by the change in the tilt angle of the molecular axis. Under an electric field, an anomalous variation with temperature in the polarization ratios has been found at the smectic A-smectic C* phase transition point.

1. Introduction. — The rotational motion about the long axis of liquid crystals has been interesting problems recently. The experimental evidence for freely rotating model has been so far reported by many authors in terephthal-bis-(p-n-butylaniline) (TBBA); for example, deuteron magnetic resonance [1] and quasielastic neutron scattering [2, 3]. An alternative model has been formulated by Meyer and McMillan [4] where the tilting of the molecules with respect to the smectic planes in the smectic C (Sm C) and Sm H phases is connected with a freezing out of the isotropic rotational motion of the molecules about their long axes. In fact, Seliger et al. [5] suggested by using 14N nuclear-quadrupole-resonance data that in the Sm C phase the molecular tilt induces the rotational bias. Moreover, Meyer et al. [6] suggested ferroelectricity in the chiral Sm C (Sm C*) phase by symmetry arguments and actually confirmed the existence of the spontaneous polarization and resulting rotational bias.

Raman scattering in liquid crystals has been extensively studied by many authors to obtain various information about phase transitions [7-9] and order parameters [10-12]. Unfortunately, however, there are not so many investigations concerning the polarized Raman scattering in aligned liquid crystals. Recently Jen et al. [11] measured the vibrational Raman depolarization ratio in uniaxial single domain nematic and smectic liquid crystals. They obtained ordinary order parameter \( \langle P_2 \rangle \) and next higher moment of the orientational distribution function \( \langle P_4 \rangle \) and discussed about molecular orientational order taking account of the biaxiality of molecules.

From a viewpoint of observing molecular rotation about the long axis by the Raman scattering, a ferroelectric liquid crystal may be one of the suitable samples. Each layer of the Sm C* phase is spontaneously polarized; the layer polarization precesses around the layer normal and is perpendicular to the tilt plane in each layer [6]. By applying electric field parallel to the smectic layer we can easily obtain the Sm C phase. Even in the Sm A phase, biased rotation of the molecule by an applied field was observed [13] in the neighboring region of the transition temperature.

To investigate the molecular rotation about the long axis, we have observed the polarized Raman scattering and its electric field effect in aligned smectic phases of (S)-2-methylbutyl p-[(p-decyloxybenzylidene)-amino]-cinnamate (DOBAMBC). Contrary to our first intention, however, our measurements of the polarization ratios are not accurate enough to investigate the molecular rotation in detail. But we obtained the characteristic temperature dependence of the polarization ratio caused by a molecular tilt and an anomalous temperature dependence of the...
polarization ratio at the Sm A-Sm C* phase transition point under an electric field. The results are reported in the following.

2. Experimental procedure. — DOBAMBC was synthesized from (S)-2-methylbutyl p-aminocinnamate and p-decyloxybenzaldehyde, which are purchased from Eastman Kodak Comp. and Tokyo Kasei Comp. Ltd., respectively. All measurements were performed by using homeotropic monodomain samples which were prepared between two glass plates treated with orienting surface agent, hexadecyltrimethylammonium bromide (HTAB). Thinly evaporated aluminium films were used as electrodes. The separation between electrodes was 2 mm.

![Diagram of two optical systems](image)

Fig. 1. — Schematic illustration of two optical systems used.

Two optical systems were used and are illustrated in figure 1. In the optical system (a), the polarized exciting light from an Ar* ion laser was passed through a sample 100 μm thick along the smectic layer, and the scattered light was observed from the direction perpendicular to the glass plate. The Ar* ion laser was operated at 514.5 nm and with 100 mW. The coordinate axes in the laboratory frame are shown in figure 1; the Z axis is normal to the smectic layer. The sample has large rotatory power for the light propagating along the Z axis in the Sm C* phase [13]. Therefore we used linearly polarized light only in the exciting light. Thus we can observe \( I_{XX} + I_{ZY} \) and \( I_{YX} + I_{YZ} \); here \( I_{ZX} \) etc. represent the polarized Raman intensities, the first subscript being the polarization direction of the incident light and the second subscript that of the scattered light.

In the optical system (b), the backward scattering is used with light propagating normal to the smectic layer. In this geometry, we cannot use linearly polarized light in the Sm C* phase because of the large rotatory power. The polarized Raman scattering was observed under applying an electric field which is large enough to unwind the helicoidal structure. By applying an electric field parallel to the X axis, the molecular axes tilt uniformly in the YZ plane. Thus we observed the polarization ratios, \( I_{XY}/I_{XX} \) and \( I_{YX}/I_{YY} \).

3. Experimental results. — Figure 2 shows the Raman spectrum of DOBAMBC in the Sm A phase. The polarization direction of the exciting light is parallel to the molecular axis. No appreciable difference in the relative intensity of the Raman bands was observed among each phase (Sm C*, Sm A and isotropic liquid phases). The Raman spectrum for N-(p-methoxybenzylidene)-p-n-butylaniline (MBBA) is also shown in figure 2 for comparison. Because of the resemblance of the molecular structures of DOBAMBC and MBBA as shown in figure 3, the main part of the spectra, that is from 1100 cm\(^{-1}\) to 1700 cm\(^{-1}\), resembles each other. The Raman spectrum of MBBA has been reported by Vergoten and Fleury [14] and the assignments of these bands has also been made. The main part of the spectrum is attributed to the vibrations of the common part of two molecules, i.e. benzene ring, \( \varphi-N \) and \( C=\equiv N \). The characteristic band of DOBAMBC appears at 1719 cm\(^{-1}\) and is attributed to the stretching vibration of CO.

![Raman Spectra](image)

Fig. 2. — Raman spectrum of DOBAMBC in the Sm A phase. Raman spectrum of MBBA is also shown for comparison.

\[
\text{[DOBAMBC]} \\
\text{C}_9\text{H}_{21}-\text{O}-\text{C}-\text{N}-\text{C}=\equiv\text{N}-\text{CH} \quad \text{[MBBA]} \\
\text{CH}_3-\text{O}-\text{C}-\text{N}-\text{C}_8\text{H}_9
\]

Fig. 3. — Molecular structures of DOBAMBC and MBBA.
The polarization ratio decreases in the Sm C* phase with increasing temperature, i.e. with decreasing tilt angle, and does not change in the Sm A phase. The absolute values of the polarization ratio are less accurate because of the experimental difficulties: in the optical system (a), the edge of the sample from which the exciting beam enters is not flat and the molecular orientation is slightly distorted at the edge. Moreover, we could not neglect a slight shift of the incident beam direction and the resulting light intensity change due to the rotation of the polarization rotator, since the beam must pass through the interstice of two glass plates.

To obtain more information for a Raman tensor, we observed the polarization ratio of the 1.593 cm\(^{-1}\) band in the optical system (b). As stated in section 2, the measurement was performed under an electric field parallel to the smectic layer. The field strength is 350 V/mm which is large enough to unwind the helicoidal structure in our temperature range measured. The result is shown in figure 4. The polarization ratios \(I_{XY}/I_{XX}\) and \(I_{XY}/I_{YY}\) are nearly equal in the Sm A phase within an experimental error, which indicates that the molecular rotation about the long axis is not affected by an electric field in the Sm A phase. The polarization ratios in the Sm A phase depend on temperature slightly and decrease with increasing temperature. This tendency has been reported in some nematic and smectic liquid crystals and is correlated with the temperature behavior of the order parameter [11]. In the Sm C phase, to which the Sm C* phase is converted by an applied field, \(I_{XY}/I_{XX}\) increases and \(I_{XY}/I_{YY}\) decreases by lowering temperature from the transition point.

As clearly seen in the figure, the anomalous structure appears at 94 °C, which nearly coincides with the transition point. The transition temperature, however, is not easy to be determined accurately for the particular sample used; for we can only measure the temperature of a copper oven in which the sample is mounted and the incident beam of 100 mW may cause the temperature difference between the irradiated part of the sample and the oven itself.

4. Discussions. — The polarization ratios in the Sm C* phase depend on temperature in a different way from those in the Sm A phase as shown in figures 4 and 5. Therefore it is reasonable to consider that the temperature dependence of the polarization ratios is mainly caused by the tilt of the molecular axis.

We will calculate the temperature dependence of the polarization ratios of the Raman intensity by taking account of the molecular tilt as a temperature dependent factor. Consider a certain Raman active vibration, of which the Raman tensor is expressed in the molecular frame as

\[
\alpha_{mol} = \begin{pmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{pmatrix}
\]

Here we used a most general form of the Raman tensor in order to include the orientational statistical fluctuation effectively in the Raman tensor. When the molecular axis tilts in the XZ plane, the Raman tensor is written in the laboratory frame of figure 1 as

\[
\alpha_{lab} = C^{-1} \alpha_{mol} C,
\]

where \(C\) is a transformation matrix and now is written as

\[
C = \begin{pmatrix}
\cos \theta & 0 & \sin \theta \\
0 & 1 & 0 \\
-\sin \theta & 0 & \cos \theta
\end{pmatrix}
\]

Here \(\theta\) is an angle between a laboratory Z axis and a molecular z axis. Then we obtain

\[
\alpha_{lab} = \begin{pmatrix}
\alpha_{xx} \cos^2 \theta - \alpha_{xz} \sin 2 \theta + \alpha_{zz} \sin^2 \theta & \alpha_{xy} \cos \theta - \alpha_{yx} \sin \theta & 1/2(\alpha_{xx} - \alpha_{zz}) \sin 2 \theta + \alpha_{xx} \cos 2 \theta \\
\alpha_{yx} \cos \theta - \alpha_{xy} \sin \theta & \alpha_{yy} & \alpha_{yz} \\
1/2(\alpha_{xx} - \alpha_{zz}) \sin 2 \theta + \alpha_{xz} \cos 2 \theta & \alpha_{yy} \cos \theta + \alpha_{yz} \sin \theta & \alpha_{xx} \sin^2 \theta + \alpha_{xx} \sin 2 \theta + \alpha_{zz} \cos^2 \theta
\end{pmatrix}
\]
The Raman intensity is, for example, expressed as

\[ I_{XY} = (\alpha_{xy} \cos \theta - \alpha_{xz} \sin \theta)^2 \]

In the optical system (a), the Raman intensity can be obtained by using a general transformation matrix and then averaging over the azimuthal angle taking account of a helicoidal structure. The same result can be easily obtained as follows; we can obtain \( \alpha_{ab} \) in the case that the molecular axis tilts in the YZ plane in the similar way as mentioned above. Then the Raman intensity in the optical system (a) is an average value of the intensity in two cases that the molecular tilts in the XZ and YZ planes respectively. Therefore

\[
2(I_{XY} + I_{YX}) = \alpha_{yy}^2 + (\alpha_{xy} \cos \theta - \alpha_{xz} \sin \theta)^2 + (\alpha_{xy} \cos \theta - \alpha_{xz} \sin \theta)^2 + (\alpha_{yy} \cos 2 \theta - \alpha_{yz} \sin 2 \theta)^2 + (\alpha_{xy} \cos 2 \theta + 1/2(\alpha_{yy} - \alpha_{xz}) \sin 2 \theta)^2 + (\alpha_{xy} \cos 2 \theta + 1/2(\alpha_{xx} - \alpha_{yz}) \sin 2 \theta)^2 .
\]

If we neglect the biaxiality of the molecule, the absolute values of the Raman tensor components can be determined by using our experimental results in the Sm A phase in the optical systems (a) and (b) and in the isotropic liquid phase in the optical system (b):

\[
|\alpha_{xx}|, |\alpha_{yy}|, |\alpha_{xz}|, |\alpha_{xy}|, |\alpha_{xz}| = (0.19, 0.19, 1, 0.16, 0.71, 0.71).
\]

We can obtain a reasonable temperature dependence of the polarization ratio in the following two cases:

\[
(\alpha_{xx}, \alpha_{yy}, \alpha_{xz}, \alpha_{xy}, \alpha_{yz}) = (-0.19, 0.19, 1, -0.16, 0.71, -0.71)
\]

or

\[
(\alpha_{xx}, \alpha_{yy}, \alpha_{xz}, \alpha_{xy}, \alpha_{yz}) = (-0.19, 0.19, 1, 0.16, -0.71, -0.71).
\]

The results are shown in figure 6, where we referred Ph. Martinot-Lagarde's [15] data to convert tilt angles into temperatures. In our calculation, we took into consideration only the tilt angle but not order parameter as a temperature dependent factor. By comparing with the experimental results, however, we can see qualitative agreements in both optical systems. Thus it is concluded that the temperature dependence of the polarization ratio mainly caused by the tilt of the molecules.

As shown in figure 5, an anomalous structure is induced by an electric field in temperature variation of the polarization ratios in the optical system (b). The reason for the appearance of the structure is not known. In our previous paper [13], the electric field induced birefringence was shown in DOBAMBC. The temperature dependence of the birefringence has sharp maximum at the transition point and may be associated to the tilt of the effective optical axis and the biased rotation of molecules. These electro-optical effect may cause the appearance of the anomalous structure in our present work. More detailed investigations are still needed and remain as future problems.

**References**


