Direct Determination of the Anisotropy of the Magnetic Susceptibility in Smectic Liquid Crystals

G. Illian, H. Kneppe, and F. Schneider
Physikalische Chemie, Universität Siegen

Z. Naturforsch. **40 a,** 46–51 (1985); received September 29, 1984

A sample of an aligned smectic liquid crystal, suspended in a magnetic field, can be excited to oscillations. Measurement of the oscillation period allows a direct determination of the anisotropy of the magnetic susceptibility. Liquid crystals exhibiting the phase sequence isotropic-nematic-smectic A can be aligned very well and precise χ_a values can be determined. A direct transformation from the isotropic to the smectic phase or phase transitions between smectic phases can cause an incomplete alignment of the liquid crystal and worse results.

Introduction

The anisotropy χ_a of the magnetic susceptibility in liquid crystals is of particular interest because it depends on the orientation of the liquid crystal and is proportional to the order parameter in perfectly aligned liquid crystals. Using the methods of Faraday or Gouy, the determination of χ_a is rather a difficult task. The forces on diamagnetic samples are very small and χ_a is only the 10% difference between the χ values in the isotropic and the liquid crystalline phase. A direct method for the determination of χ_a would therefore be advantageous.

As the torque on the director in a magnetic field is proportional to χ_a, static and dynamic methods can be developed for samples in which the director is fixed to the sample vessel. In the static method the torque on the director can be determined by measuring the torsion of a suspension wire or by using Krishnan's flip angle method. As the torque on the sample has to be exerted for a long time, the director orientation will not remain fixed to the vessel for smectic samples with comparatively low viscosities and a creeping of the equilibrium position results. This disadvantage can be avoided in the dynamic method in which the sample oscillates in a magnetic field (oscillating sample magnetometer). This method has been previously used to determine the anisotropy of the susceptibility of ferromagnetic materials [1, 2] and even of high viscous nematic liquid crystals [3]. The simple set-up, the permanent torque reversion and the precise determination are advantages as compared with the static methods.

Experimental

The experimental set-up is shown schematically in Figure 1. The sample tube T (high precision NMR sample tube with 1.5 cm diameter) contains up to 12 cm^3 of the degassed liquid crystal C and is suspended from the glass rod R and the torsion wire W (tungsten wire, 1 m length, 30 μm diameter). Period and amplitude of the sample oscillation can

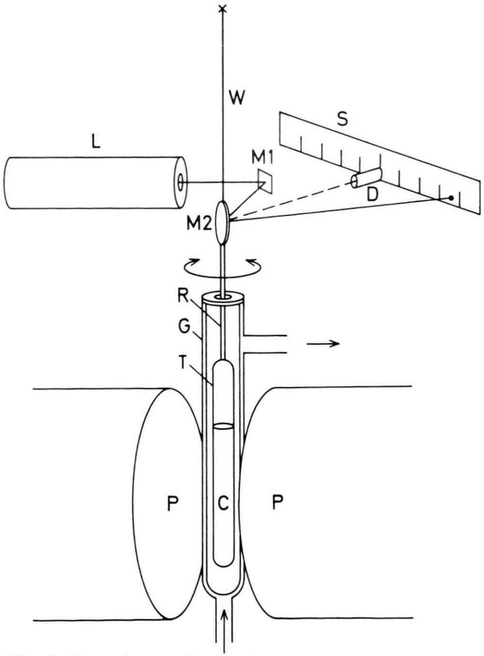

Fig. 1. Experimental set-up.

Reprint requests to F. Schneider, Physikalische Chemie, Universität Siegen, Postfach 10 12 40, 5900 Siegen.

0340-4811 / 85 / 0100-0046 $ 01.30/0. – Please order a reprint rather than making your own copy.

4′-cyano-4-n-octylbiphenyl	8CBP	S_A 33.7 N 41 I
4,4′-di-n-pentylbiphenyl	55BP	S_E 46 S_B 52 I
4′-n-hexyloxyphenyl-4-n-octyloxybenzoate	–	K 54.6 S_C 65.6 N 89.3 I
4′-n-butyloxybenzylidene-4-n-butylaniline	4O·4	S_G 42.7 S_B 45.3 S_A 46.1 N 75.3 I
4′-n-pentyloxybenzylidene-4-n-butylaniline	5O·4	S_G 52.1 S_A 52.5 N 69.2 I
4′-n-hexyloxybenzilidene-4-n-butylaniline	6O·4	S_G 56.5 S_B 58.6 S_A 69.4 N 77.3 I
4′-n-heptyloxybenzylidene-4-n-butylaniline	7O·4	S_G 62.5 S_C 65.0 S_A 73.8 N 76.3 I
4′-n-octyloxybenzylidene-4-n-butylaniline	8O·4	S_G 63.5 S_B 67.5 S_A 81.2 I

be determined by means of the laser L, the two mirrors M1 and M2, the scale S and the photodiode D which is coupled to an electronic clock. The sample is placed between the pole shoes of an electromagnet (20 cm pole shoe diameter, 3 cm pole gap, 0–1.5 T) and surrounded by a double-walled glass tube G which is kept at constant temperature within ± 0.02 K by means of a water thermostat.

Measurement of the field strength is performed with a Hall probe which is calibrated with an NMR Gaussmeter. The moment of inertia of the sample is determined by comparing the oscillation period of the sample at 0 T with that of an aluminium cylinder with known moment of inertia.

The liquid crystals used in this investigation are either commercial products (4′-cyano-4-n-octylbiphenyl from BDH) or are synthesized according to well-known reactions. Transition temperatures (in °C) and acronyms for the liquid crystals are shown in the Table.

Theory

The oscillation of the sample is studied under the following assumptions.

I There is no motion of the liquid crystal with respect to the sample tube. The axis of alignment (director) is fixed relative to the sample tube and the orientation is uniform and perpendicular to the oscillation axis.

II The torsion of the wire as well as the magnetic torque vanish in the equilibrium position.

III Damping can be neglected.

Then, the energy balance can be written as

$$\tfrac{1}{2} I \dot{\varphi}^2 + \tfrac{1}{2} D \varphi^2 + \tfrac{1}{2} \frac{\chi_a B^2 V}{\mu_0} \sin^2 \varphi = \tfrac{1}{2} D \varphi_{\max}^2 + \tfrac{1}{2} \frac{\chi_a B^2 V}{\mu_0} \sin^2 \varphi_{\max} \,, \tag{1}$$

where φ denotes the angle between field direction $\boldsymbol{B}$ and director $\boldsymbol{n}$ ($\varphi = 0$ in the equilibrium position), I the moment of inertia, D the torsion constant of the suspension wire and V the sample volume. For small angles φ and small ratios of torsional to magnetic torque, φ can be replaced by $\sin \varphi$

$$\dot{\varphi}^2 = \left(\frac{D}{I} + \frac{\chi_a B^2 V}{\mu_0 I} \right) (\sin^2 \varphi_{\max} - \sin^2 \varphi) \,. \tag{2}$$

The oscillation period is obtained by integration

$$\int_0^{\varphi_{\max}} \frac{d\varphi}{\sqrt{\sin^2 \varphi_{\max} - \sin^2 \varphi}} = \frac{1}{4} \left(\frac{D}{I} + \frac{\chi_a B^2 V}{\mu_0 I} \right)^{1/2} T \,. \tag{3}$$

The substitution $\sin \varphi / \sin \varphi_{\max} = \sin \psi$ leads to a complete elliptic integral of the first kind

$$K(\sin \varphi_{\max}) = \frac{1}{4} \left(\frac{D}{I} + \frac{\chi_a B^2 V}{\mu_0 I} \right)^{1/2} T \,. \tag{4}$$

Series representation of K and introduction of the angular frequency $\omega = 2\pi/T$ leads to

$$\omega_r^2 = \frac{D}{I} + \frac{\chi_a V}{\mu_0 I} B^2 \,, \tag{5}$$

$$\omega_r = \omega (1 + \tfrac{1}{4} \sin^2 \varphi_{\max} + \tfrac{9}{64} \sin^4 \varphi_{\max} + \ldots) \,, \tag{6}$$

where the reduced angular frequency ω_r is the angular frequency for vanishing amplitude $\varphi_{\max}$. A plot of ω_r^2 versus B^2 should therefore give a straight line with a slope from which χ_a can be calculated. The moment of inertia can be directly determined from the angular frequency at $B = 0$ according to $D/I = \omega^2$.

The method described above can be used for uniaxial smectic liquid crystals (S_A or S_B) as well as for biaxial liquid crystals (S_E, S_G etc.). For biaxial liquid crystals, the susceptibility tensor exhibits three different components (χ_1, χ_2 and χ_3) in a properly chosen coordinate system. If the axis of highest susceptibility χ_1 is parallel to the direction of the magnetic field in the equilibrium position of the sample and if there is no preferred orientation of the other axes, $\chi_{\parallel} = \chi_1$ and $\chi_{\perp} = \tfrac{1}{2}(\chi_2 + \chi_3)$ results. Therefore, the anisotropy is $\chi_a = \chi_1 - \tfrac{1}{2}(\chi_2 + \chi_3)$.

Difficulties arise when measuring χ_a in S_C phases. If the S_C phase is formed from a nematic or smectic

A phase in the presence of a strong magnetic field, the director will be aligned parallel to the magnetic field direction. The smectic layers are tilted by the tilt angle with different azimuthal angles. In contrast to liquid crystals with director orientations perpendicular to the layers, the director can rotate on cones around the layer normal if the sample is excited to oscillations.

Numerical calculations on the basis of the Hornreich-Shtrikman [4] model show that one can distinguish three different cases.

I If the characteristic time for the director alignment on the cone is short as compared with the oscillation period, a small damping of the oscillation amplitude is expected. For small amplitudes, the dependence $\omega_r^2 = f(B^2)$ is still linear. Depending on the direction of the layer normal, the director can follow the magnetic field direction in a varying degree. This effect reduces the effective χ_a by a factor of 2.

II If the characteristic time and the oscillation period are comparable, a large damping should be observed. Generally, the dependence $\omega_r^2 = f(B^2)$ will be non-linear. The small number of oscillations will prevent an accurate measurement of the oscillation period.

III If the characteristic time is much larger than the oscillation period, the director rotation becomes very small for all sample oscillation amplitudes and χ_a can be determined by means of (5).

Testing

In order to ensure correct operation of the set-up, we have performed the following tests: Dependence of the angular frequency on the oscillation amplitude, linearity of the plot ω^2 versus B^2, flow of the liquid crystal with respect to the sample tube and asymmetry of the sample tube.

The reduction of the angular frequency ω according to (6) is shown in Figure 2. We observe constant ω_r values within the error for the determination of the oscillation amplitude. Figure 3 shows the experimental verification of (5). With thin suspension wires, the precise linear dependence of ω_r^2 on B^2 is even fulfilled for small inductions (0.01 T). Deviations, which are due to the approximations used in the derivation of (5), are only observed with thicker wires (150 µm iron wire) and at inductions smaller than 0.1 T.

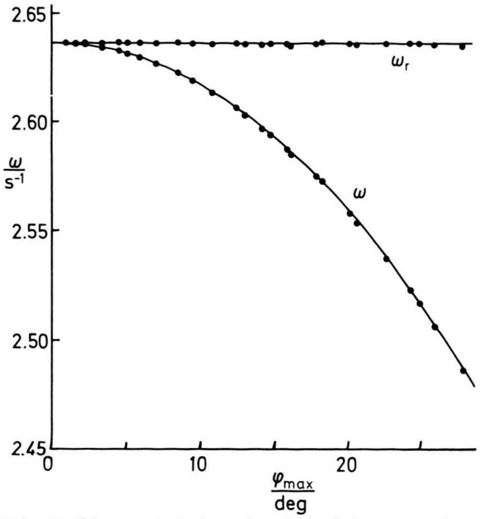

Fig. 2. Observed (ω) and reduced (ω_r) angular frequency as a function of the oscillation amplitude φ_{max} (8CBP, 25 °C, 0.8 T). The ω curve is calculated from (6) assuming a constant value for ω_r.

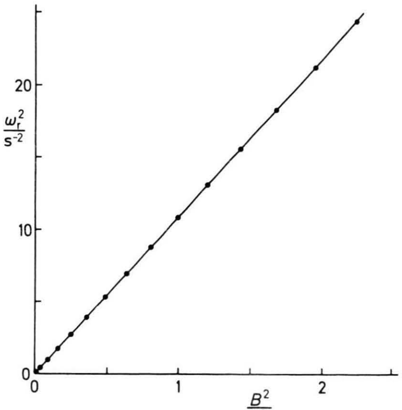

Fig. 3. Reduced angular frequency ω_r squared as a function of the induction B squared for 8CBP at 25 °C.

If a flow of the smectic liquid crystal takes place with respect to the sample tube during the oscillation, (5) is no longer valid for the determination of χ_a. This flow of the liquid crystal can be detected by measuring the equilibrium position of a sample on which a magnetic torque is exerted. In order to get a strong torque on the sample we used an induction of 1.55 T and a 150 µm iron wire. Figure 4 shows the observed variation of the orientation of the sample as a function of time after changing the direction of the magnetic field by 33.5 °. The torsion angle ξ of the suspension wire at the beginning of

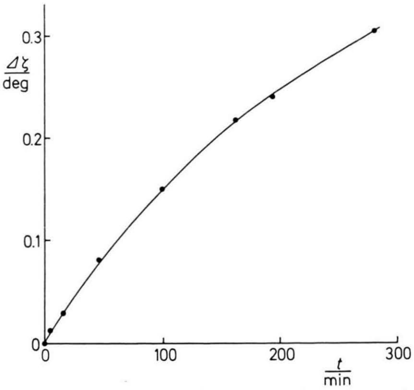

Fig. 4. Change $\Delta\xi$ of the sample orientation as a function of time after application of a magnetic torque of $1.8 \cdot 10^{-6}$ Nm on 8CBP at 25 °C. The sample is suspended from a wire with $D = 3.5 \cdot 10^{-6}$ Nm.

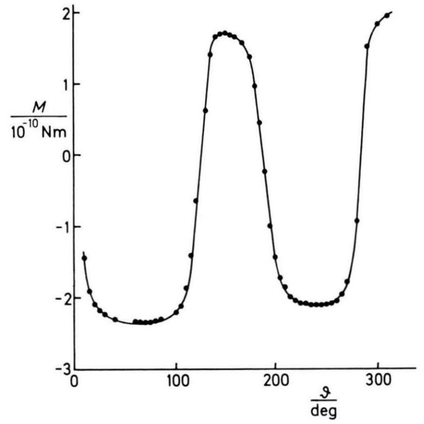

Fig. 5. Torque M on an isotropic sample (8CBP above the clearing point) as a function of the angle ϑ between field direction and an arbitrarily defined direction of the sample at 1.5 T.

the experiment amounts to 30.3° which corresponds to a torque of $1.8 \cdot 10^{-6}$ Nm. The experiment shows that the director rotation during an oscillation period is very small and that the influence of a possible flow of the liquid crystal can be neglected.

Furthermore, a lower limit for the apparent rotational viscosity γ_1 in the S_A phase can be derived from this measurement. A value of $3 \cdot 10^6$ Pa·s is obtained for 8CBP at 25 °C. This value is four orders of magnitude larger than the limit presented by Dong [5]. A further confirmation of the fixed director orientation with respect to the sample tube is the very small damping of the oscillation which amounts to $4 \cdot 10^{-3}\,\mathrm{s}^{-1}$. The independence of this quantity on the field strength shows that it is mainly caused by the viscosity of the surrounding air.

All quantities for the determination of χ_a with this method can be measured with high accuracy. These quantities are: oscillation period of the sample, induction of the magnetic field, mass or volume of the liquid crystal, torsion constant of the suspension wire and moment of inertia of the sample. The temperature dependence of the torsion constant of the tungsten wire ($1 \cdot 10^{-4}\,\mathrm{K}^{-1}$) can be normally neglected.

The measurement of small anisotropies and the accuracy of measurement is limited by imperfect axial symmetry of the sample tube and inhomogeneity of the magnetic field. The influence of these effects can be easily observed by measuring the torques which are exerted on the sample at different orientations of the rotable electromagnet (Fig. 5), if the sample tube is filled with an isotropic liquid (8CBP above the clearing point). In order to avoid a dependence of the equilibrium orientation of the sample on the field strength, the χ_a measurements were performed at a sample orientation with zero deflection. Neglect of the torques due to the sample anisotropy leads to a relative error of about $1 \cdot 10^{-4}$ in χ_a.

Results and Discussion

The major problem in measuring χ_a values in smectic liquid crystals is the alignment of the liquid crystal. Generally, the alignment is obtained by cooling down a sample in a strong magnetic field from the isotropic phase via other liquid crystalline phases to the desired smectic phase. Our measurements show that the effective anisotropy $\chi_{a,\mathrm{eff}}$ of the magnetic susceptibility depends strongly on the experimental conditions during this cooling process. The best results, i.e. the smallest scattering of χ_a values, are obtained if the liquid crystal exhibits the phase sequence isotropic-nematic-smectic A.

The alignment in the S_A phase of 8CBP was studied as a function of the cooling rate. It turned out that the highest anisotropies, i.e. the best alignment, were obtained with the highest cooling rates. This may be due to the fact that at low cooling rates the smectic phase grows from a few nuclei at the wall of the sample. Because of the surface alignment these nuclei may not be aligned in the direction of the magnetic field. At high cooling rates nucleation is spread over the whole sample which results in a better alignment. Even at high cooling rates we found a dependence of $\chi_{a,\,\mathrm{eff}}$ on the induction of the magnetic field during the cooling process. In Fig. 6 $\chi_{a,\,\mathrm{eff}}$ is plotted versus $B^{-1/2}$ giving a nearly linear dependence. However, a dependence on B^{-1} which is expected for a nematic phase cannot be excluded because of the scattering of the values at low inductions. Extrapolation to infinite induction gives a χ_a value which is 3% (1% for the B^{-1} dependence) larger than $\chi_{a,\,\mathrm{eff}}$ at 1.5 T. This extrapolation is not used in the following determinations.

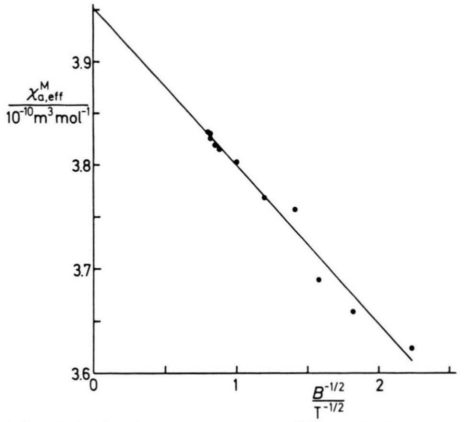

Fig. 6. Effective anisotropy $\chi^{M}_{a,\,\mathrm{eff}}$ of the molar magnetic susceptibility of 8CBP at 29 °C as a function of the inverse square root of the magnetic induction during the cooling process.

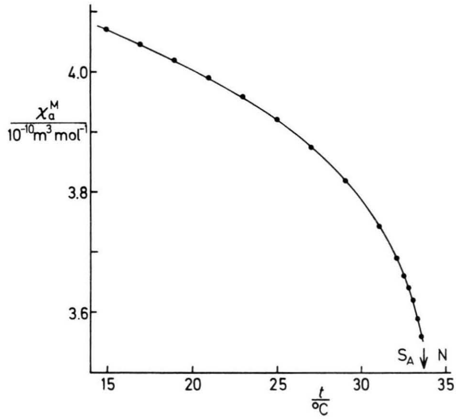

Fig. 7. Temperature dependence of the molar susceptibility anisotropy of 8CBP.

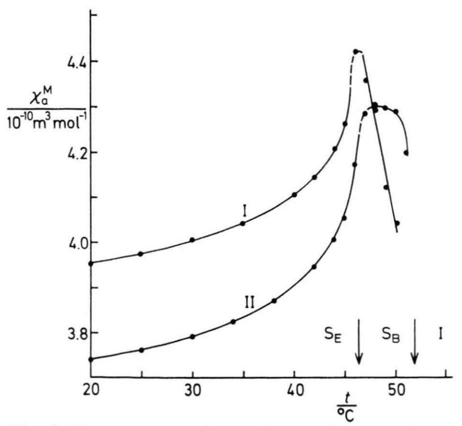

Fig. 8. Temperature dependence of the molar susceptibility anisotropy of 55BP for two samples (I: 5 g, II: 11 g 55BP).

The temperature dependence of χ_a is presented for 8CBP in Figure 7. The values agree very well with those reported by Sherell and Crellin [6]. The increase in χ_a with decreasing temperature is probably due to the increasing order parameter.

4,4′-Dipentylbiphenyl exhibits the phase sequence isotropic – smectic B – smectic E. As this liquid crystal does not exhibit a nematic phase, it has to be aligned during the phase transition isotropic-smectic B. A large series of experiments showed that the best alignment was obtained at maximum field strength and very low rates of cooling in the order of 0.1 K/h. Even under these conditions the χ_a values scatter between 60 and 100% of the highest value. The alignment could be improved by increasing the temperature of the smectic sample for a short time giving an isotropic phase in the outer region of the sample and cooling down again. This improvement may be due to a better alignment of the center of the sample after the first cooling and an extension of this alignment to the outer regions of the sample during the second cooling process. Nevertheless, the χ_a values presented in Fig. 8 are only tentatively. The transition to the S_E phase is coupled with a strong increase in density. Cracks are formed in the sample and a funnel-shaped depression of the free surface is observed. Furthermore, it was observed that the decrease in $\chi_{a,\,\mathrm{eff}}$ at the transition to the S_E phase is reduced for samples with smaller filling height. As χ^{M}_{a} should remain constant or increase at transitions between orthogonal phases, the decrease is probably due to the mechanical processes which can cause a breaking up of the sample into domains with slightly different alignment. This effect can only be avoided in very flat samples which are unfavourable for the measurement because of sample volume and accessible field strength, resp.

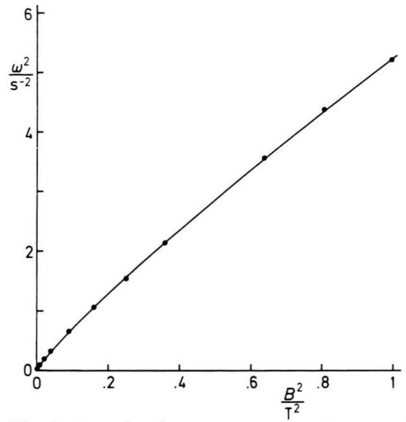

Fig. 9. Angular frequency squared versus induction squared for 4′-n-hexyloxyphenyl-4-n-octyloxybenzoate at 65 °C in the S_C phase.

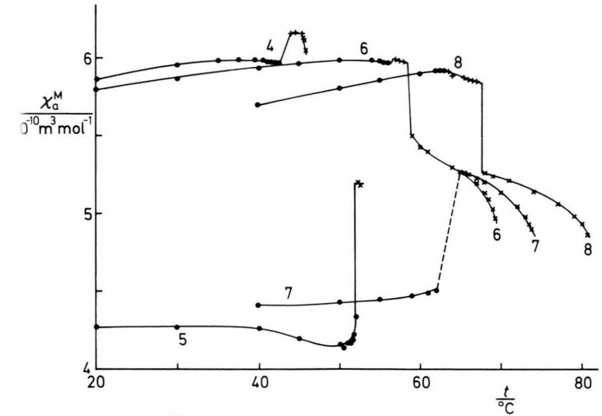

Fig. 10. χ_a^M for some 4′-n-alkoxybenzylidene-4-n-butylanilines as a function of temperature. Chain lengths are indicated at the curves. Smectic phases are denoted as follows: S_A: x, S_B: +, S_C: --- (not measured, only as a guide for the eye), S_G: ●.

The measurement of χ_a in S_C phases can only be performed under favourable conditions. Usually, the rotation of the director leads to a very strong damping of the oscillation and one has to start with large amplitudes in order to get one or two oscillations. Figure 9 shows the dependence $\omega^2 = f(B^2)$. Because of the director rotation the calculation of ω_r is not feasible. The bending of the curve is only slightly reduced by plotting $\omega^2 + \delta^2$ versus B^2 (δ = damping) or by using measurements at small field strengths which lowers the damping. The determination of χ_a is therefore not possible.

The behaviour of χ_a in other smectic phases was studied in the series of 4′-n-alkyloxybenzylidene-4-n-butylanilines (Figure 10). This series has already been studied by Hardouin et al. [7] who found χ_a values about 20% lower except 6 O · 4 for which a 20% higher value was found. Our values show a systematic variation within the series. The members with an even number of carbon atoms in the alkyl chain which exhibit the phase sequence $S_A - S_B - S_G$ give high χ_a values in the low temperature phase S_G. The odd members 5 O · 4 and 7 O · 4 for which the S_B phase is missing or replaced by an S_C phase give lower χ_a values. Assuming nearly equal order parameters for the compounds, the degree of alignment in 8O·4 is nearly as high as in 6O·4 and 4O·4 though the nematic phase is missing in 8O·4. In the orthogonal S_A and S_B phases a continuous increase of χ_a with decreasing temperature is observed. Probably, this is caused by an increase in the order parameter. The behaviour in the S_G phase is varying. 5O·4 and 7O·4 show a strong decrease at the phase transition whereas 4 O · 4, 6 O · 4 and 8 O · 4 show mostly a slight decrease in χ_a with falling temperature. Probably, this is not caused by an increase of the tilt angle but rather a result of the motion in the sample. The damping of the sample oscillation is very small in the S_G phases, i.e. a director rotation in this tilted phase is not possible under these conditions.

In conclusion, we have demonstrated that the oscillating sample method gives very precise values for the effective χ_a of smectic samples. The major problem is the preparation of perfectly aligned samples. S_A phases with a high temperature nematic phase can be aligned very well. Missing of a nematic phase or transitions between smectic phases generally lead to a worse alignment. A statement on tilt angle and/or order parameter in highly ordered smectic phases is therefore not possible from χ_a measurements.

[1] G. W. Rathenau and J. L. Snoek, Physica **8,** 555 (1941).
[2] H. Zijlstra, Rev. Sci. Instrum. **32,** 634 (1961).
[3] G. Heppke and F. Schneider, Z. Naturforsch. **28 a,** 994 (1973).
[4] R. M. Hornreich and S. Shtrikman, Solid State Commun. **17,** 1141 (1975).
[5] R. Y. Dong, Mol. Cryst. Liq. Cryst. **72,** 59 (1981).
[6] P. L. Sherrell and D. A. Crellin, J. Physique **40,** C3–211 (1979).
[7] F. Hardouin, M. F. Achard, G. Sigaud, and H. Gasparoux, Mol. Cryst. Liq. Cryst. **39,** 241 (1977).