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Preliminary communication

NEXAFS measurements of the molecular ordering in the boundary layers of liquid crystalline free standing films

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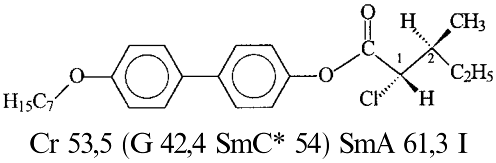
By near edge X-ray absorption fine-structure (NEXAFS) spectroscopy a finite molecular tilt angle in the surface layer of a free standing film in the liquid crystalline smectic A phase of C7 was directly detected. Analysis of the angular dependent intensities of the oxygen K edge NEXAFS spectra leads to an average tilt angle of the molecules in the surface layer of about 34°, which is characteristic for the bulk smectic C* phase of C7.

Ferroelectricity exists in chiral liquid crystalline smectic C (SmC*) phases. Since these systems are used in various display devices, knowledge of the ferroelectric properties is very important for the development of liquid crystal display technology. It is well known that in the smectic A phase of liquid crystal materials the local director is oriented perpendicularly to the smectic planes, whereas in smectic C phases it is tilted with respect to the layer normal by a certain angle θ. This is found for the bulk phases. In a free standing film (FSF) of a smectic A phase, however, there are indications that the director of the boundary layers also is tilted [1–7].

The first indication for a tilt of the molecules in the boundary layers of a smectic A phase was reported by Heinekamp *et al.* [1] and in some more detail by Amador and Pershan [2] in the case of *p*-decyloxybenzylidene-*p*-aminocinnamaic acid 2-methylbutyl ester (DOBAMBC) by means of ellipsometry. In free standing films of C7, Bahr and Fliegner obtained a finite tilt angle above the SmA/SmC bulk transition temperature, also deduced from ellipsometry results [3]. It should be stressed that ellipsometry is an integral method that assumes a mean field model in order to interpret the data. Kraus *et al.* [4] concluded that a tilt was present in the boundary layers of a SmA FSF from measurements of the reflectivity and by polarizing microscopy. The spontaneous polarization in a FSF of the SmA phase of C7 found by Hoffmann and Stegemeyer [5, 6], as well as the detection of a Goldstone mode in an ultrathin SmA FSF by Becker and Stegemeyer [7] have also been discussed by assuming a tilt in the boundary SmA layers.

These indications were all obtained by indirect experimental methods. In this paper we used NEXAFS measurements, in partial yield electron detection mode, as a surface sensitive method to probe directly the molecular orientation in the surface layer of a FSF prepared *in vacuo* and maintained *in vacuo* during the measurements. By this direct method we clearly demonstrate that in a FSF there is indeed a molecular tilt in the surface layer of the smectic A phase. Note that the following results are related to the first outer smectic layer of the film.

The NEXAFS experiments were carried out with the chiral smectic liquid crystal 4-(3-methyl-2-chloropentanoyloxy)-4′-heptyloxybiphenyl (C7) [3] which readily forms stable FSFs homogenising within a few minutes. The molecular structure is given below together with the phase transition temperatures (in °C).



Cr 53,5 (G 42,4 SmC* 54) SmA 61,3 I

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The FSFs were drawn in a copper frame with one movable edge in an upright position. In order to avoid the destruction of the film by sudden vacuum application, the film was drawn under high vacuum conditions (10^{-6} mbar). The frame was electrically heated by a tungsten wire. The NEXAFS spectra were recorded in partial yield mode (retarding voltage of − 100 V) at the storage ring BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung mbH, Berlin) using the high energy plane grating monochromator PM 6. The experimental resolution was better than 1 eV at the O 1*s* edge. The raw spectra were normalized to the incident photon flux using a spectrum obtained from a GaAs-diode.

The orientation of the molecules in the surface layers of a FSF of C7 were now investigated by NEXAFS spectroscopy [8]. In figure 1 the normalized NEXAFS spectra at the O K-edge recorded at different angles between the synchrotron beam and a FSF of C7 are shown. As the temperature of the frame was 63°C (± 2°C) during the experiments, the film could be kept in the smectic A phase. The spectra show a sharp peak at 531.5 eV (see figure 1) which can be assigned to an excitation into the $\pi^*_{O=C}$ orbital of the carbonyl oxygen of the ester group [9, 10]. It would be anticipated that C7 shows only one π^* type resonance in the O K edge spectrum, as it contains one doubly bonded O atom. However, the spectra reveal an additional sharp peak at 534.5 eV just below the ionization edge. Similar observations have been reported in the literature [10–12]. There are several possible explanations for such a transition. Due to the close proximity between the single bonded oxygen atom of the ether and the ester bridge with the phenyl rings, it might be possible to excite directly from the O1*s* into the π^* orbital of the phenyl ring as was discussed by Keil *et al.* for a polycarbonate film [12]. This explanation is to some extent supported by the fact that poly(*p*-phenyl ether) shows a similar resonance although it lacks a double bonded oxygen atom [12]. However, Hitchcock *et al.* have measured the same effect by electron energy loss spectroscopy for ethyl benzoate where the proximity argument given above should not apply [10]. Lippitz *et al.* attribute a similar result for poly(bisphenol A carbonate) film to bond–bond interactions of the carbonyl π system [13]. This interpretation is corroborated by the fact that the angular dependence of this resonance correlates with the energetically lowest $\pi^*_{C=O}$ resonance at 531.5 eV.

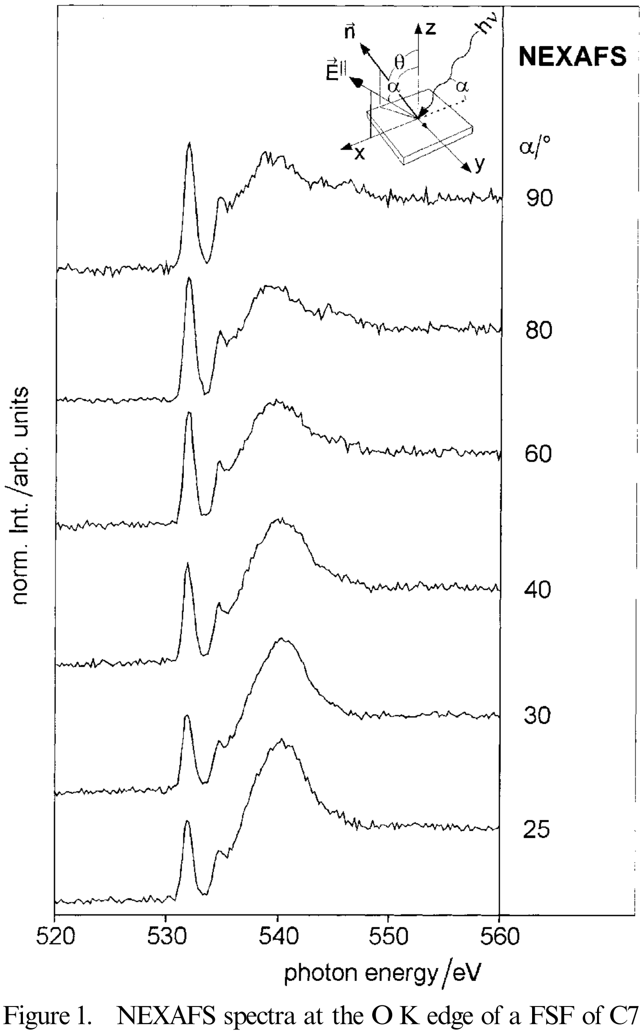

Figure 1. NEXAFS spectra at the O K edge of a FSF of C7 in the SmA phase ($T = 63 \pm 2$°C) for various angles α between the synchrotron beam and the surface of the FSF. The film thickness if approximately 100 smectic layers, recording time about 3 min.

From the broad structures above, approximately 536 eV can be assigned to so-called σ^* resonances. According to the literature it is most likely that the intense peak at approximately 540 eV is due to excitations into the $\sigma^*_{C=O}$ resonances of the two oxygen bridges (ether, ester) [10, 13]. The weak peak at 545 eV can be assigned to an excitation into the $\sigma^*_{C=O}$ resonance of the carbonyl group [10].

According to the decrease in the intensities of the two π^* resonances in figure 1 with decreasing angle (α) between the incident synchrotron light and the film plane, one can conclude directly that the molecules are preferably in an out-of-plane orientation (tilt angle lower than about 45°), because the transition dipole moment (TDM) of the carbonyl group should be orthogonal to the long axis of the molecule. This conclusion is corroborated by the reverse angular dependence of the σ^* resonances at approximately 540 eV as the TDM of the σ^* resonances should be preferably oriented along the long axis of the molecule. Accordingly the σ^* resonance at 545 eV which has been assigned to the $\sigma^*_{C=O}$ resonance decreases in intensity with decreasing angle α as is expected for the proposed geometry.

In order to determine a tilt angle θ of the molecules with respect to the surface normal, it is necessary to evaluate the intensities of the different resonances. A quantitative measurement of the intensities of the σ^* resonances is hampered by the fact that a precise knowledge of the different dipole transitions—their energy, position and orientation with respect to the molecular framework—is missing. The determination of the intensity of the peak at 534.5 eV is difficult because of the close energetic vicinity between this peak and the absorption edge whose energetic position is uncertain.

Therefore we have determined the intensities of the lowest π^* resonance at 531.5 eV with respect to the angle α. Figure 2 shows the π^* resonance intensities as a function of the angle α between the incoming light and plane of the FSF. Additionally we have plotted theoretical curves which have been calculated for different molecular tilt angles θ under the assumption that the molecules have no azimuthal order. This assumption is justified by the following arguments. The diameter of the synchrotron beam is about 2–3 mm and hence larger than the smectic domains. Although there is a homogeneous tilt within the domains, its azimuthal order is averaged out under our experimental conditions. The calculations were performed according to equations presented by Stöhr *et al.* [14] assuming a polarization of the synchrotron radiation P of 0.85. A comparison of the experimental data with the theoretical curves shown in figure 2 gives an average molecular tilt in the boundary layer of $\theta \approx 34°$ with an uncertainty of a few degrees. Within the experimental accuracy this is just the same tilt angles as that found in bulk SmC* phases of C7 [15].

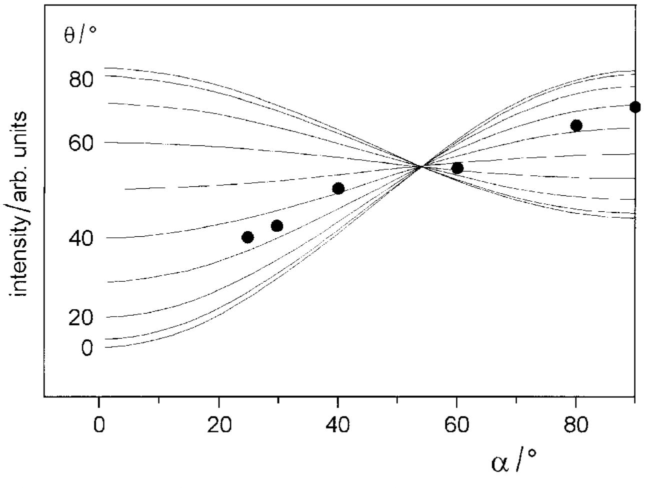

Figure 2. Experimental and theoretical dependence of the intensity of the NEXAFS peak at 531.5 eV on the angle α between the synchrotron beam and the surface of the FSF. The solid lines are theoretical curves calculated for different molecular tilt angles θ. The dots are experimental data.

In summary, the molecular tilt in the boundary layers of FSFs of a smectic A phase, proposed on the basis of various indirect experimental techniques [1–4], was directly observed by NEXAFS spectroscopy. The measured tilt angle of 34° is in good agreement with the tilt angle in the SmC* bulk phase [15]. Our results provide evidence that the molecular orientation in the first surface layer of a smectic A FSF must be described by a tilted structure which is caused by surface tension [16]. With this point in mind, these experiments were carried out under high vacuum conditions where it can be certain that the atmosphere around the FSF has no influence on the molecular ordering in the surface layer.

As shown by model calculations [17], the molecular tilt is not retricted to the first surface layer but penetrates into the film over a rather short length of less than about 10 layers [16, 17]. Consequently, the ferroelectric switching [5, 6] and the Goldstone mode [7, 18] observed in the smectic A phase of a FSF are caused by tilted smectic C* layers and take place in a boundary region at the liquid crystal/air interface into which the tilt penetrates.

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