# Observation of a soft smectic liquid-crystal phase in a mixture showing V-shaped switching

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We present the experimental observation of a soft smectic liquid crystal phase in a three-component liquid crystal mixture reported to exhibit V-shaped switching. Unlike the layer compression modulus $B$ of the usual smectic phase, $B$ of the soft smectic phase has a peculiar temperature and frequency dependence. It was found that this characteristic feature is one of the main driving force to realize an ideal V-shaped switching.

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## I. INTRODUCTION

Until now, various tilted fluid smectic liquid crystal phases have been found [1]. Particularly, since the discovery of tristable switching [2] between the antiferroelectric chiral smectic-$C_A^*$(Sm-$C_A^*$) phase and the ferroelectric chiral smectic-$C^*$(Sm-$C^*$) phase, much attention has been paid to clarifying the structure and origin of the emergence of Sm-$C_A^*$ [1]. In the course of the extensive research with antiferroelectric liquid crystals, various ferrielectric subphases were discovered in the temperature range between the smectic-$A$ (Sm-$A$) and the Sm-$C_A^*$ [3] phases. The appearance of subphases indicated that several interlayer orderings can be stabilized in liquid crystal phases without long-ranged intralayer positional order [3].

Conversely, the recent discovery by Fukuda and coworkers [4,5] of a so-called thresholdless antiferroelectricity *seemed* to suggest the reduction of the interlayer orderings. At first, a thresholdless, hysteresis-free, domain-free, V-shaped electrooptic response was observed in thin homogeneous cells of a three-component mixture of chiral smectic liquid crystals [4]. V-shaped switching has attracted considerable attention because of its fundamental interest and a strong demand to realize attractive liquid crystal displays with high speed response, extremely wide viewing angle, and high contrast ratio [4–14].

This switching was first speculated to occur in a phase with randomly oriented C directors due to the reduction of the interlayer tilting correlation [4,5]. The dynamic switching behaviors were explained by a random model based on a two-dimensional Langevin function under the strong influence of electric field and surface conditions [8–10]. More recently, Park *et al.* proposed a model, i.e., the highly coherent azimuthal angle rotation model (collective model). They claimed that a collective model is much more appropriate to interpret experimental results in V-shaped switching than a random model [11,12]. Even now, however, important unsettled questions remain about the nature and driving force of V-shaped switching. The authors of Refs. [11–13] tried to explain the nature of V-shaped switching by the effect of the polarization charge. However, experimental results were not enough to explain this by taking into account the effect of the polarization charge. Park *et al.* also commented on the softening of the liquid crystal system [11]. They speculated that the softening of the system may influence the effect of the polarization charge through an elastic constant, and realize V-shaped switching. There is still no evidence that a liquid crystal mixture showing V-shaped switching is soft. Also, even now, the softening of a smectic liquid crystal phase by means of elastic constant measurements has never been observed.

In this way, much attention has been paid to the nature of V-shaped switching. Meanwhile, the mechanical property of the mixture showing V-shaped switching is not understood at all. In this paper, we present measurements of the layer compression modulus of the material showing V-shaped switching, and discuss the nature of V-shaped switching.

## II. EXPERIMENT

The materials studied were a three-component mixture used in the original and recent works of V-shaped switching [5,10–13], and the smectic liquid crystal materials *not* showing V-shaped switching; 10BIMF7 and 10BIMF8 [15]. The molecular structures and the phase sequences are shown in Fig. 1, where Iso, Ferri, Sm-$X^*$, and AF represent the isotropic, ferrielectric, smectic-$X^*$, and antiferroelectric phases, respectively. V-shaped switching was observed in the phase designated as Sm-$X^*$ in thin homogeneous cells. The assignment of the Sm-$X^*$ phase is now controversial: the Sm-$X^*$ phase has been reported to be a Sm-$C^*$ phase [13] or, alternatively, to be a ferrielectric phase [10]. We can compare the results of the mixture showing V-shaped switching [Fig. 1(a)] with those of the usual smectic liquid crystals 10BIMF7 [Fig. 1(b)] and 10BIMF8 [Fig. 1(c)]. For measuring the layer compression modulus $B$, we prepared homeotropically aligned cells consisting of two glass plates treated with a surfactant. Using piezoelectric ceramics, the longituidinal mechanical transfer function $Z(\omega)$ was measured over a frequency range from 20 to 500 Hz. $Z(\omega)$ is defined as the ratio of the complex stress experienced by a receiving glass plate to the complex longituidinal strain of a driving glass plate. Based on continuum theory, $Z(\omega)$ can be expressed as $Z(\omega)=B+i\omega(\eta_1-\eta_2+\eta_4+2\eta_5)$ [16], where $\eta_1$, $\eta_2$, $\eta_4$, and $\eta_5$ are the Martin-Parodi-Pershan viscosity coefficients

 

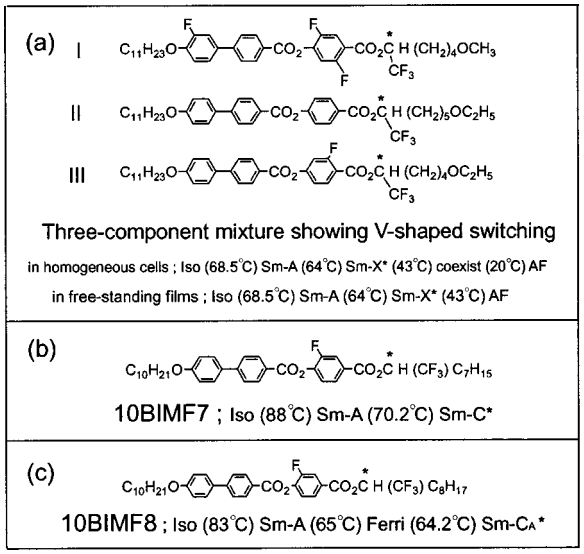


FIG. 1. Molecular structures and phase sequences of (a) a three-component mixture showing V-shaped switching with a ratio of I:II:III=4:4:2, (b) 10BIMF7, and (c) 10BIMF8.

[17]. Our experimental setup is a modified version of the original system developed by Cagnon and Durand [18]. The details of our system were reported elsewhere [19].

### III. RESULTS AND DISCUSSION

First we present results near the normal Sm-*A* to Sm-*C** and Sm-*A* to ferrielectric phase transition. Figure 2 shows the temperature dependences of *B* in liquid crystals 10BIMF7 (closed circles) and 10BIMF8 (open circles). *B* is the extrapolated value at the zero frequency in Figs. 2 and 3. *B* shows the critical softening near the phase transition from Sm-*A* to Sm-*C** phases and from Sm-*A* to ferrielectric phases, and then steeply increases with decreasing temperature. These cusplike behaviors of *B* are generally observed near the phase transition from the untilted Sm-*A* to tilted smectic phases; i.e., Sm-*A*–Sm-*C**, Sm-*A*–Sm-$C_A^*$, Sm-*A*–Sm-$C_\alpha^*$, and Sm-*A*–ferrielectric phases [20–22].

On the other hand, *B* of the material showing V-shaped switching exhibits an unusual temperature dependence. Figure 3 shows the temperature dependence of *B* in a three-component mixture showing V-shaped switching. *B* shows an evident critical softening near the phase transition from Sm-*A* to Sm-*X**, as is usually observed. This substantial pretransitional effect reflects the diminishing of the restoring force on the tilt fluctuations [20–22]. Below the Sm-*A*–Sm-*X** phase transition, *B* stays in a low level, and gradually increases with decreasing temperature in contrast to *B* of 10BIMF7 and 10BIMF8 in Fig. 2. In the vicinity of the Sm-*X**–AF phase transition, *B* increases steeply. So far such a kind of remarkable change of *B* near the phase transition between smectic phases has never been observed, to our knowledge. Since the AF phase can be regarded as the usual smectic phase [10,12], we consider that the Sm-*X** phase is an unusual soft phase. The abrupt increase of *B* near the Sm-*X**–AF phase transition can be explained by the recovery of layer elasticity in the usual smectic phase. This can also be confirmed by the fact that the temperature dependence of *B* in the AF phase can be extrapolated to *B* in the Sm-*A* phase.

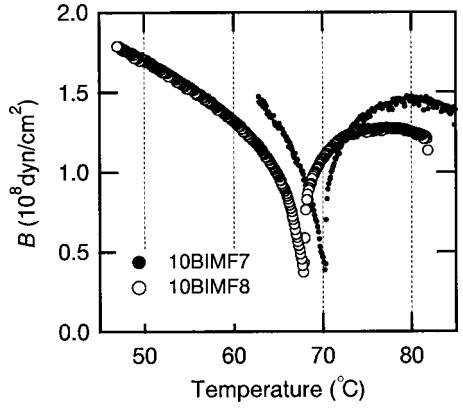


FIG. 2. Temperature dependence of *B* in 10BIMF7 (closed circles) and 10BIMF8 (open circles).

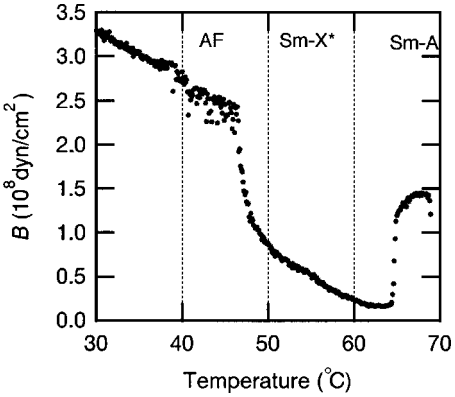


FIG. 3. Temperature dependence of *B* in the three-component mixture showing V-shaped switching.

Let us consider the origin of the softening of the smectic phase. For one thing, we can consider the possibility of a diminishing or weakening of the interlayer tilt correlation. As noted previously, V-shaped switching was first speculated to occur in a phase with randomly oriented C directors due to the reduction of the interlayer tilting correlation [4,5]. However, the molecular motion during V-shaped switching can be explained by the collective model more reasonably than the random model [11,12]. Also, in the temperature range showing V-shaped switching in thin cells, the selective reflection due to the helicoidal structure is observed in a free-standing film [10]. Recently, Panarin *et al.* [23] claimed to observe a random disordered ferroelectric tilted smectic phase in the second compound of a three-component mixture showing V-shaped switching [Fig. 1(a)-II]. We measured the temperature dependence of *B* of this sample. In the random smectic phase claimed by Panarin *et al.*, however, we only observed typical behavior. A more detailed description of this observation will be presented in a future publication. Consequently, the unusual behavior of *B* in the soft phase cannot be explained by only the disordered director distribution.

What is more, we have to note the possibility of the bi-

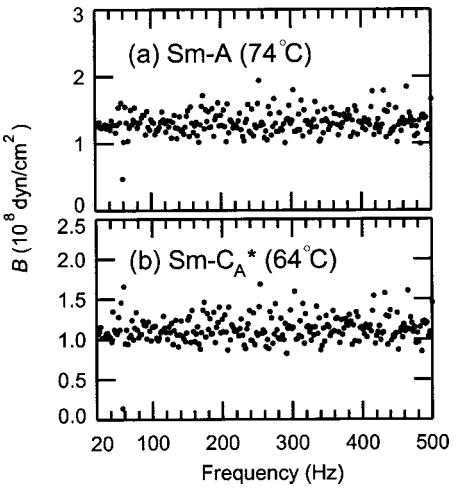


FIG. 4. Frequency dependence of $B$ in 10BIMF8 (a) in the Sm-$A$ phase and (b) in the Sm-$C_A^*$ phase.

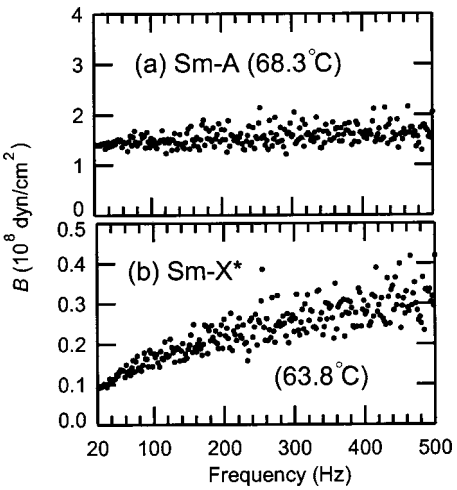


FIG. 5. Frequency dependence of $B$ in the three-component mixture showing V-shaped switching, (a) in the Sm-$A$ phase, and (b) in the Sm-$X^*$ phase.

layer and partial bilayer tilted smectic phases. However, the temperature dependence of $B$ near the smectic-$A_2$–smectic-$A_d$ phase transition is dissimilar to our result, where smectic-$A_2$ and smectic-$A_d$ phases are bilayer and partial bilayer nontilted smectic phases, respectively [24]. Moreover, x-ray measurements allow us to rule out the possibility of bilayer and partial bilayer phases [25]. Furthermore, it seems reasonable to suppose that the diminishing of the bond orientational order is not the origin of the softening. Viewed in this light, the origin of the softening may be ascribed to the diminishing of the order of the layer structure induced by the very short correlation length or for some other reason. There is room for argument on this point, and it needs further investigation.

Next we studied the frequency dependence of $B$. Figure 4 shows the frequency dependence of $B$ in 10BIMF8 in the Sm-$A$ phase (a) and in the Sm-$C_A^*$ phase (b). $B$'s in the Sm-$A$ phase as well as the Sm-$C_A^*$ phase are independent of the frequency. In the case of 10BIMF7, the same behaviors are also observed in the Sm-$A$ and Sm-$C^*$ phases. In this frequency range, such a behavior has been generally observed even near the phase transitions [19–21]. In contrast to the results of 10BIMF7 and 10BIMF8, we observed an uncommon behavior in the material showing V-shaped switching. Figure 5 shows the frequency dependence of $B$ in the three-component mixture showing V-shaped switching, in the Sm-$A$ phase (a) and in the Sm-$X^*$ phase (b). $B$ in the Sm-$A$ phase exhibits a negligible dependence on the frequency, while $B$ in the Sm-$X^*$ phase depends strongly on the frequency. This frequency dependence of $B$ suggests that there exists a type of low frequency relaxation mode against the layer compression in the Sm-$X^*$ phase. We consider that the typical stiff response appears in a high frequency region, because this low frequency relaxation process can be completely frozen against fast layer compression. In a like manner, the relaxation phenomenon in the Sm-$X^*$ phase from the electric field may be different from that in the usual phase.

We shall now discuss the mechanism of V-shaped switching. V-shaped switching is characterized by an almost uniform orientation of molecules at zero field and by collective molecular motion during the switching [11,12]. The effect of the polarization charge was suggested to explain the uniform orientation [11,13]. Experimental results, particularly the high contrast ratio, cannot be explained only by taking into account the effect of the polarization charge from the standpoint of the elastic energy [26]. However, it was revealed in the present study that the layer in the Sm-$X^*$ phase is extremely soft. The soft layer system, which allows the existence of a steep layer twist, may contribute to compensate for the loss of the elastic energy, and contribute to realizing the uniform orientation by polarization charge interaction. Actually, a steep layer twist near substrate surfaces was observed in attenuated total internal reflection measurements, which will be represented in a separate paper [27]. In addition to the softness of the system, the relaxation phenomenon in the Sm-$X^*$ phase is different from that in the usual phase.

## IV. CONCLUSION

We reported the temperature and frequency dependences of the layer compression modulus of a liquid crystal mixture showing V-shaped switching. We observed a softening of the smectic phase in a Sm-$X^*$ phase showing V-shaped switching. The softening of the smectic phase can be attributed to the disorder of the layer structure. Moreover, it was also found that $B$ in the soft smectic phase has a characteristic frequency dependence which is relevant to the relaxation time. The softening of the system, and particularly the relaxation phenomenon due to the external force, have a strong influence on the polarization charge effect, and contribute to realizing ideal V-shaped switching.

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