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X-ray diffraction study of ferroelectric and antiferroelectric liquid crystal mixtures exhibiting de Vries SmA^*-SmC^* transitions

U. Manna,[1] R. M. Richardson,[2] Atsuo Fukuda,[1] and J. K. Vij[1,*]

[1]*Department of Electronic and Electrical Engineering, Trinity College, University of Dublin, Dublin 2, Ireland*

[2]*H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, United Kingdom*

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In this Rapid Communication, results on smectic layer thickness, using synchrotron radiation x-ray diffraction, for different mixtures of ferroelectric and antiferroelectric liquid crystals are given. We find that with an increased ferroelectric component in the mixtures, the layer shrinkage at the de Vries SmA^*-SmC^* transition increases. This observation can be used to explain our previously observed behaviors [U. Manna, J.-K. Song, Yu. P. Panarin, A. Fukuda, and J. K. Vij, Phys. Rev. E **77**, 041707 (2008)] that the soft-mode dielectric strength decreases, the Landau coefficient increases, and the Curie-Weiss temperature range decreases with increased ferroelectric component in the mixture exhibiting de Vries SmA^*-SmC^* transition.

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I. INTRODUCTION

The simplest structure of the Sm-A^* phase assumes that the smectic layer spacing (d_A) is equal to the molecular length L. If we assume perfectly ordered rodlike molecules with director tilt θ, the smectic layer spacing in the SmC^* phase (d_C) is reduced to

$$d_C = d_A \cos\theta. \tag{1}$$

In 1970s, x-ray experiments on SmA phase of a number of achiral compounds carried out by Diele *et al.* [1], suggested that the smectic layer spacing d_A is 5–10 % lower than the calculated length L of the mesogenic molecules which may lead to a constant layer spacing with decreasing temperature. Based on these experimental results, Adrian de Vries suggested that in these materials, the molecular long axis and presumably the local director is tilted through a finite angle, but azimuthally uniformally distributed with $f(\varphi)=1/2\pi$ on a cone from layer to layer as well as in a single layer [2–4], with the macroscopic director pointing along the layer normal. Recently, Landau theory of smectic phases was developed to show that de Vries behavior occurs in materials with unusually low orientational order [5,6], which has been experimentally demonstrated [7–9]. Recently, it was also shown that the molecules in the de Vries SmA^* possess a local orientational order indeed even without the application of the electric field, i.e., the molecules are not randomly oriented but orient with a finite correlation length which is of the order of a few tens of nm, and these molecules cooperatively respond to the applied electric field [10].

In our previous paper [11], mixtures with different compositions of an antiferroelectric liquid crystal (AFLC) compound, that exhibits direct SmA^*-SmC_A^* transition with a ferroelectric compound (FLC), the latter exhibits only SmA^*-SmC^* transition, were studied using electro-optics and dielectric spectroscopy. The results of optical micrograph, birefringence and the apparent tilt angle measurements suggested that a part of the SmA^* phase is of de Vries type since an increase in the tilt angle with decreasing temperature results in a reduction in the value of the birefringence within SmA^* phase, whereas the birefringence at SmA^* to SmC^* transition goes up by 12.7%. The soft-mode relaxation strength, the Landau coefficient of the temperature-dependent term and the other related parameters of the de Vries-types SmA^*-SmC_A^* and SmA^*-SmC^* transitions were determined using Landau theory for the second-order phase transition. For the SmA^*-SmC^* transition, it was found that the soft-mode relaxation strength decreases, the Landau coefficient increases and the Curie-Weiss temperature range decreases with an increased ferroelectric component in the mixture.

In this Rapid Communication, we add synchrotron radiation x-ray diffraction results to those given in our previous paper [11]. We find that with increased ferroelectric component in the above mentioned mixtures, the layer shrinkage at the de Vries SmA^*-SmC^* transition increases. For low layer shrinkage materials, the restoring force of the tilt-angle fluctuations is smaller, which explains the previously observed behaviors.

II. RESULTS AND DISCUSSIONS

The small-angle x-ray scattering (SAXS) experiments were carried out using the ID02 station at the European Synchrotron Radiation Facility, Grenoble. In these experiments, a monochromatic x-ray beam is incident on the temperature controlled sample and the scattering pattern is recorded on a two-dimensional detector. A wavelength of 0.75 Å was used and the two-dimensional charge coupled device (CCD) detector was positioned to give a Q range of 0.02–0.9 Å^{-1}. The samples were contained in 1.5-mm-diameter Lindemann glass tubes which were placed in an electrically heated sample environment box. The raw data were regrouped to intensity vs scattering vector using the standard software of the ID02 instrument and the smectic layer spacings were determined from the center of gravity of the first-order layer reflection peaks [12]. Smectic layer spacings for the three different mixtures of the AFLC MC-881 and FLC MC-815 were also determined as a function of composition, i.e., ferroelectric to antiferroelectric ratio in the mixtures. The

*jvij@tcd.ie

TABLE I. The compositions, phase sequences and order of transitions of different mixtures of MC-881 and MC-815.

MC-881	$SmC^*_A \xrightarrow[112.5\ °C]{1st}$ $SmA^* \xrightarrow[120\ °C]{1st}$ Is
MC-815	$SmC^* \xrightarrow[96\ °C]{1st}$ Is
88MC881 (12% MC-815+88% MC-881)	$SmC^*_A \xrightarrow[109.3\ °C]{1st} SmC^* \xrightarrow[110.5\ °C]{1st}$ $SmA^* \xrightarrow[120\ °C]{1st}$ Is
80MC881 (20% MC-815+80% MC-881)	$SmC^*_A \xrightarrow[105.7\ °C]{1st} SmC^* \xrightarrow[110\ °C]{1st}$ $SmA^* \xrightarrow[120\ °C]{1st}$ Is
72MC881 (28% MC-815+72% MC-881)	$SmC^*_A \xrightarrow[89\ °C]{2nd} SmC^* \xrightarrow[108\ °C]{2nd}$ $SmA^* \xrightarrow[120\ °C]{1st}$ Is

compositions and the phase sequences of the mixtures are shown in Table I.

The result of the temperature-dependent smectic layer spacing measurement of the mixture 80MC881 is shown in Fig. 1. The smectic layer spacing of the compound 80MC881 is compared to the layer spacing that would be expected according to Eq. (1) when the optically observed tilt angle is taken into account. The comparison illustrates that the layer shrinkage is actually occurring in this material. However, the layer shrinkage is smaller than the shrinkage which is expected by the conventional picture of "tilting rodlike molecules." This confirms that the mixture under study (80MC881) can be classified as a "de Vries-type" material even though the picture is not of an ideal de Vries scenario which would have zero layer shrinkage. The inset of Fig. 1 shows the variation in smectic layer spacing in the temperature range corresponding to the SmA^* phase. Initially in the SmA^* phase, the layer spacing increases with decreasing temperature due to an increase in the orientational order parameter. In the temperature range corresponding to the de Vries-type SmA^* phase, the macroscopic order parameter, measured by the layer spacing is lower than in the conventional SmA^* phase because of the existence of a molecular tilt with random azimuthal distribution. The existence of an increased molecular tilt with decreasing temperature results in a reduction in the value of the layer spacing within the de Vries-type SmA^* phase as shown in the inset of Fig. 1. This is in agreement with the temperature-dependent birefringence in the SmA^* phase given in Ref. [11].

In our previous paper [11], the Landau parameters associated with the SmA^*-SmC^* transition in three different mixtures of ferroelectric and antiferoelectric compounds were calculated from dielectric measurements using Landau theory of the second-order phase transition with increased ferroelectric component in the mixtures. The results of the smectic layer spacing of the same three different mixtures are shown in Fig. 2. One notices from Fig. 2 that the layer spacing shows a step at the SmC^*-SmC^*_A for the 88% and 80% mixtures of MC881 and a kink for the 72% mixture of MC881 in MC815. These also show that the transitions are first order though these tend to go toward the second order with an increase in the concentration of the ferroelectric compound MC815. Song *et al.* [13] from their tilt angle measurements showed that the transitions in the pure compounds are at least first order. For 88MC881, 80MC881 and 72MC881 the layer shrinkages at the SmA^* to SmC^* transition are around 2.5%, 3%, and 3.5%, whereas the layer shrinkages at the SmC^* to SmC^*_A transition are 1.3%, 0.07%, and 0.06%, respectively. Hence, it is noted that with increased ferroelectric (or decreased antiferrielectric) component in the mixtures, the layer shrinkage at the SmA^* to SmC^* transition increases because of a strong coupling between the tilt and the layer thickness, whereas the layer shrinkage at the SmC^* to SmC^*_A transition decreases much more significantly. Because of a stronger coupling between the tilt and the layer thickness at the SmA^* to SmC^* transition, we need larger elastic energy to change the director tilt for larger layer shrinkage materials. Since the major part of the restoring force to the tilt-angle fluctuations is the elastic

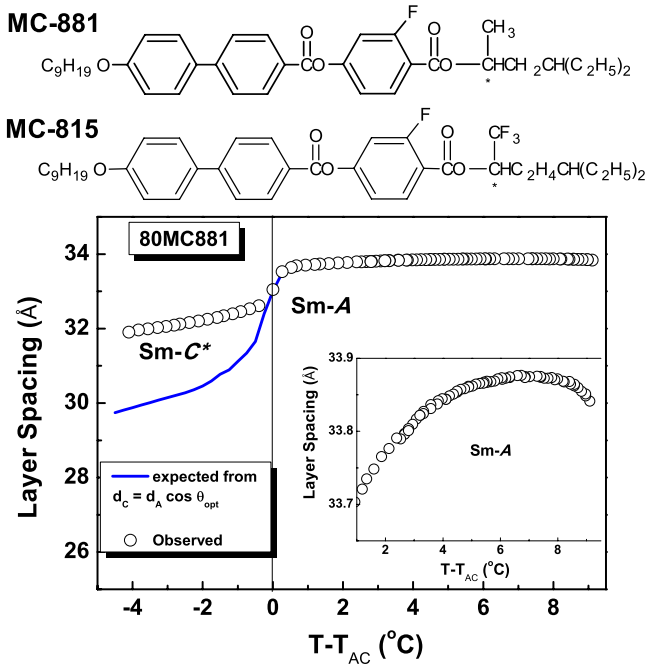

FIG. 1. (Color online) Structural formulas of MC881 and MC815 with the transition temperatures given in Table I. Temperature-dependent smectic layer spacing d of 80MC881 (80% MC881 and 20% MC815) at SmA^*-SmC^* transition. The actual d values experimentally observed by SAXS are compared with the hypothetical values which are expected from the optical tilt angle in the SmC^* phase according to Eq. (1). The inset shows the temperature-dependent smectic layer spacing in the SmA^* phase.

energy associated with tilt-induced changes in the smectic layer spacing, the restoring force of the tilt angle fluctuations for larger layer shrinkage materials is greater. As a result, the soft-mode dielectric relaxation strength decreases, Landau coefficient α increases and the Curie-Weiss temperature range decreases at the de Vries-type SmA^*-SmC^* transition with increased ferroelectric component in the mixture [11,14]. Note that the experimental observation is different as expected from a "simple picture" where the intermolecular forces drive the molecules into layers and these forces determine the layer spacing, and if the layers spacing is very strongly defined, then increasing temperature will just reduce the correlation between the azimuthal angles within a layer, changing the phase from SmC^* to SmA^*. In this case, the soft-mode fluctuations would be weaker as the polar angle would be very strongly defined contrary to our experimental observations.

III. CONCLUSIONS

The results of the x-ray diffraction measurements show that the mixtures of ferroelectric and antiferroelectric liquid crystals exhibit de Vries-type SmA^* phase. The layer shrinkage at the SmA^*-SmC^* transition is smaller than the shrinkage expected from the conventional picture of tilting rodlike molecules in one of the studied mixtures. It has also been shown that with increased ferroelectric component in the mixtures of the AFLC MC-881 and FLC MC-815, the layer shrinkage at the SmA^*-SmC^* transition increases. These results explain our previous observations that with increased ferroelectric component in the mixture, the soft-mode dielectric relaxation strength decreases, Landau coefficient α increases, and the Curie-Weiss temperature range decreases at the de Vries-type SmA^*-SmC^* transition. A steplike change in the layer thickness is observed at the SmC^* to SmC_A^* transition which in turn indicates a steplike change in the tilt angle for the 88% and 80% mixtures of the antiferroelectric and ferroelectric compounds. From the layer thickness measurements, both SmA and SmC^* and SmC^*-SmC_A^* transitions in the mixtures with higher antiferroelectric components are found to be first order. The findings support the view that de Vries behavior and antiferroelectricity in liquid crystals are linked to each other through the same underlying physical mechanism of weak correlations among the neighboring tilt directions, as shown recently by Sandhya *et al.* [15].

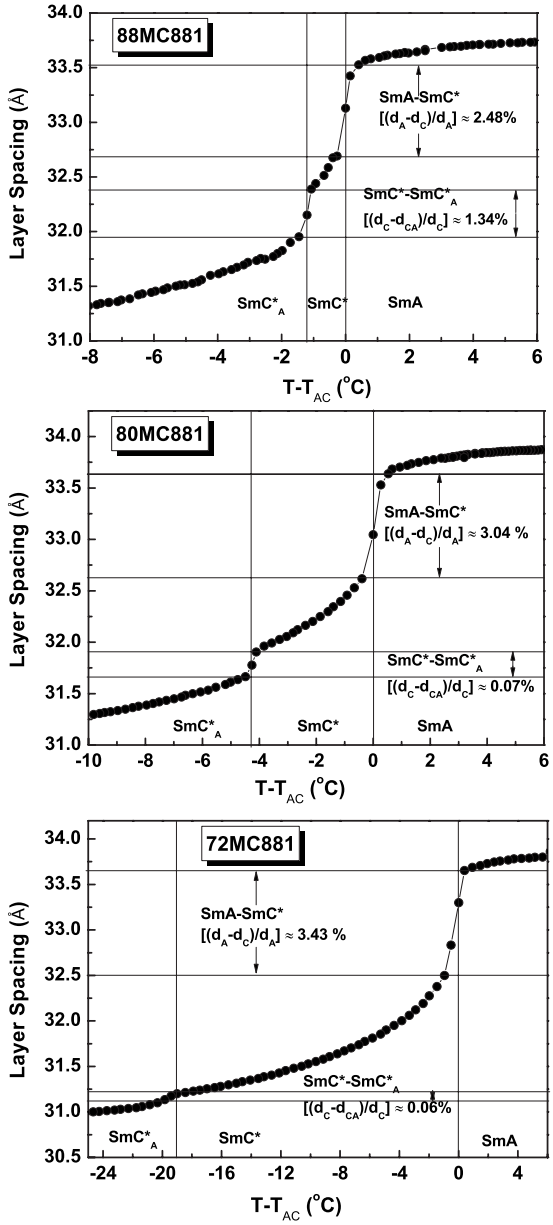

FIG. 2. Layer shrinkage at the SmA^* to SmC^* and SmC^* to SmC_A^* transitions with increased (decreased) ferroelectric (antiferroelectric) component in the mixture.

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