Electrooptic Observation of the Goldstone and Soft Modes near the SmA-SmC_A* Phase Transition

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Abstract

In order to investigate the details of the molecular fluctuation behavior around the SmA-SmC_A* phase transition point, we have carried out electrooptic measurements in 4-(1-trifluoromethylheptyloxy-carbonyl)phenyl-4'-octyloxybiphenyl-4-carboxylate, which undergoes a phase transition directly from SmA to SmC_A*, as functions of temperature and frequency. The relaxation due to the Goldstone mode was clearly observed in the SmC_A* phase. We found that the optical signal due to the Goldstone mode vanishes at a certain temperature in the antiferroelectric SmC_A* phase. The helix distortion due to the antiferroelectric Goldstone mode excited by an electric field is discussed.

I. INTRODUCTION

Several years ago, Chandani *et al.* discovered a new liquid crystalline phase bearing close resemblance to the smectic C* phase in (*R*)-4-(1-methylheptyloxycarbonyl)phenyl-4'-octyloxybiphenyl-4-carboxylate(MHPOBC) [1, 2]. The novel phase has an antiferroelectric ordering and a double helical structure. Molecules in neighboring layers tilt in the same direction and the opposite sense, so that the dipole moments are canceled out within the two adjacent layers, and the tilt direction precesses around the smectic layer normal to form a helical structure. The novel phase was designated as smectic C_A* (SmC_A*), using a subscript A standing for "antiferroelectric" [3-5].

There exist two characteristic fluctuation modes in the chiral smectic liquid crystals; the Goldstone mode associated with the fluctuation of azimuthal angle around the helical axis and the soft mode described as the fluctuation of the molecular tilt angle. Neither of the Goldstone and soft modes in SmC_A* seems to be observable by dielectric measurements, because the spontaneous polarization vanishes. However, the soft mode contribution to the dielectric constant has observed around the SmA-SmC_A* phase transition point in several antiferroelectric liquid crystals [6-8]. This discrepancy implies that there exists the fluctuation of the ferroelectric mode as well as the antiferroelectric one in the SmC_A* phase [9-12]. In the antiferroelectric soft mode, the directors in neighboring layers fluctuate in the same direction but the opposite sense, so that no polarization is brought about. However, the ferroelectric soft mode, namely the tilt fluctuation

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distorting the antiferroelectric ordering, brings about macroscopic polarization. Note that the antiferroelectric soft mode is associated with the change of layer thickness, whereas the layer thickness change cancels out within two adjacent layers in ferroelectric soft mode.

As for the Goldstone mode in the SmC$_A$* phase, few dielectric measurements have been successful in detecting the relaxation, because the symmetry-recovering Goldstone mode corresponds to the antiferroelectric phase mode bringing about no macroscopic polarization [8, 13]. The details of the relaxation behavior of the Goldstone mode in the antiferroelectric SmC$_A$* phase were unknown, though the existence had been distinguished by photon correlation spectroscopy [14-16]. Recently, the relaxation process of the antiferroelectric Goldstone mode was clearly observed through electrooptic responses to a sinusoidal electric wave. The frequency of the optical signal due to the antiferroelectric Goldstone mode is twice as high as that of applied ac fields, because the distoriton of the helix is caused by a dielectric anisotropy [13, 17].

In this paper, the relaxation behavior around the SmA-SmC$_A$* phase transition is investigated by means of electrooptic measurements. We measured the temperature and frequency dependences of the optical response due to the Goldstone and soft modes in an antiferroelectric liquid crystal, TFMHPOBC. It was confirmed that the relaxation behavior of the antiferroelectric Goldstone mode was clearly observed in SmC$_A$*, using the electrooptic measurements. The amplitude of the optical signal due to the Goldstone mode was found to vanish at a certain temperature in the antiferroelectric SmC$_A$* phase. We will report the experimental details and discuss the fluctuation of the antiferroelectric Goldstone mode excited by an electric field [18].

II. EXPERIMENT

The sample used was (*S*)-4-(1-trifluoromethylheptyloxycarbonyl)-phenyl-4′-octyloxybiphenyl-4-carboxylate (TFMHPOBC),

$C_8H_{17}O$-⬡-⬡-COO-⬡-COO*CH(CF_3)C_6H_{13}.[19]

The material shows the following phase sequence in the cooling process:

Iso-(122°C)-SmA-(110°C)
-SmC$_A$*-(60°C)-Cryst.

The transition temperatures listed above are by DSC, and those in sandwich cells seriously depend on cell thickness. The material was sandwiched between glass plates separated by 7 μm thick spacers. The glass plates were coated ITO as electrodes. For homogeneous alignment, the glass plates were coated with polyimide (Toray Industry, SP510) and one of them was rubbed unidirectionally.

In electrooptic measurements, the optical response under a sinusoidal electric wave was observed by a photomultiplier (Hamamatsu, R955) attached to a polarizing optical microscope [13]. The signal was detected by a lock

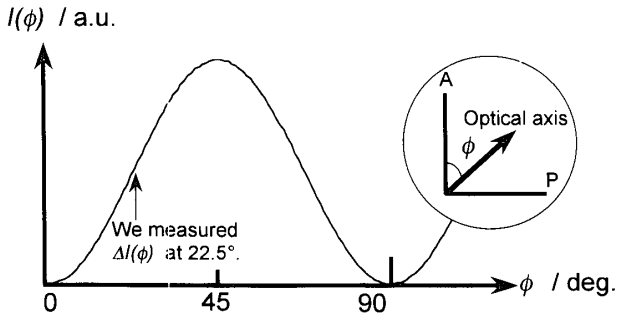

Fig. 1 The transmitted light intensity I through the homogeneous aligned cell is described as eq. (1), where ϕ is the angle of the optical axis with respect to one of the polarizer direction. A linear response between I and ϕ is obtained at ϕ=22.5°.

-in amplifier (NF, 5610B). The transmitted light intensity I through the sample cell of the thickness d placed between crossed polarizers is described as

$$I = I_0 \sin^2(2\phi)\sin^2(\pi d\Delta n/\lambda), \quad (1)$$

where ϕ is the angle of the optical axis with respect to one of the polarizer directions, Δn the difference between the long and short axes of the projection of the index ellipsoid onto the glass surface, and λ the incident light wave length. As shown in Fig. 1, we measured the light intensity at $\phi = 22.5°$ where a linear response between I and ϕ is obtained. The incident light of 546 nm was selected using an interference filter. The measuring field was 0.6 Vrms/μm and no biased field was applied in this measurement.

The sample cell was mounted in a Mettler FP82 microfurnace for temperature regulation. The lock-in amplifier and the temperature regulator were controlled by a microcomputer (NEC, PC9801RA), so that the optical response in the frequency range between 10 Hz and 120 kHz was automatically measured while the temperature was changed by 0.2°C increments.

III. RESULTS

In order to investigate the details of the helix fluctuation process, we tried to detect the change of the transmitted intensity I through the homogeneously aligned cell. Figure 2 shows a projection model of the helix fluctuation excited by an electric field in the SmC_A^* phase. Please notice that the frequency of the helix distortion caused by the dielectric anisotropy must be two times higher than that of the applied electric field wave. The helix fluctuation is accompanied with the change of Δn, so that the transmitted light intensity I is modulated at frequency $2f$ under the sinusoidal

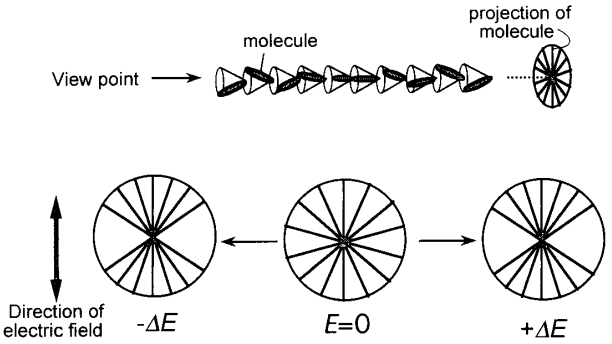

Fig. 2 A projection model of the helix fluctuation excited by an electric field in the SmC_A^* phase. Since the helix distortion is caused by the dielectric anisotropy, the frequency of the helix fluctuation must be two times higher than that of the applied electric field wave.

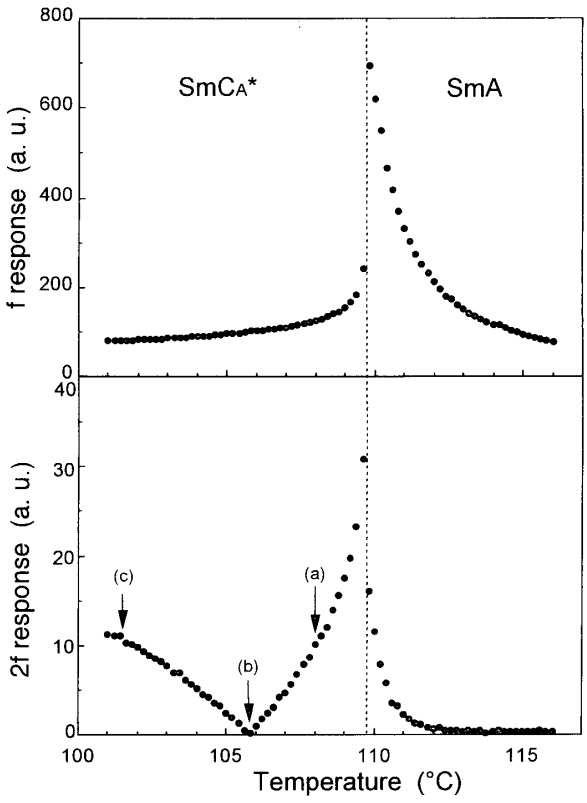

Fig. 3 Temperature dependence of optical signal of f and $2f$ response to an applied electric field of frequency 200 Hz in (*S*)-TFMHPOBC. Optical signal was measured in cooling process. A vertical dotted line indicates the transition temperature from SmA to SmC_A^*.

electric field of the frequency of f. On the contrary, the change of the optic axis, namely the distortion of the antiferroelectric ordering,

would give a modulation of the same frequency f as the applied field [13].

We show the temperature dependence of the optical signal of f and $2f$ response measured at 200 Hz in Figure 3. A vertical dotted line indicates the transition temperature from SmA to SmC$_A$*. The measuring frequency was chosen low enough to allow measurements of both the contribution of the Goldstone and soft modes in the material used. We instantly recognize the ferroelectric soft mode contribution in f response. The strength of the f response increases gradually with decreasing temperature in SmA until it attains a maximum and abruptly decreases in SmC$_A$*. Since the transition from SmA to SmC$_A$* in TFMHPOBC is of the first order, the strength of the f response jumps at the phase transition temperature. This soft mode behavior of the optical response agrees with that of the dielectric constants already reported [7].

We also recognize the $2f$ signal above SmA-SmC$_A$* phase transition point. We can point out that the ferroelectric soft mode as well as the antiferroelectric one may contribute to $2f$ response in the SmA phase. But the details remain to be worked out in the future, since the relaxation behavior observed is complicated and unclear.

Below the SmA-SmC$_A$* phase transition temperature, the signal strength of the $2f$ response decreases with decreasing temperature until it vanishes at 105.8°C (arrow (b) in Fig. 3). With a further temperature decrease, the $2f$ response increases. Note that there is no such anomaly in the temperature dependence of the f response in the SmC$_A$* phase. In addition, the relaxation frequency of the $2f$ response is almost independent on temperature in the SmC$_A$* phase, as we shall see later in the follow-

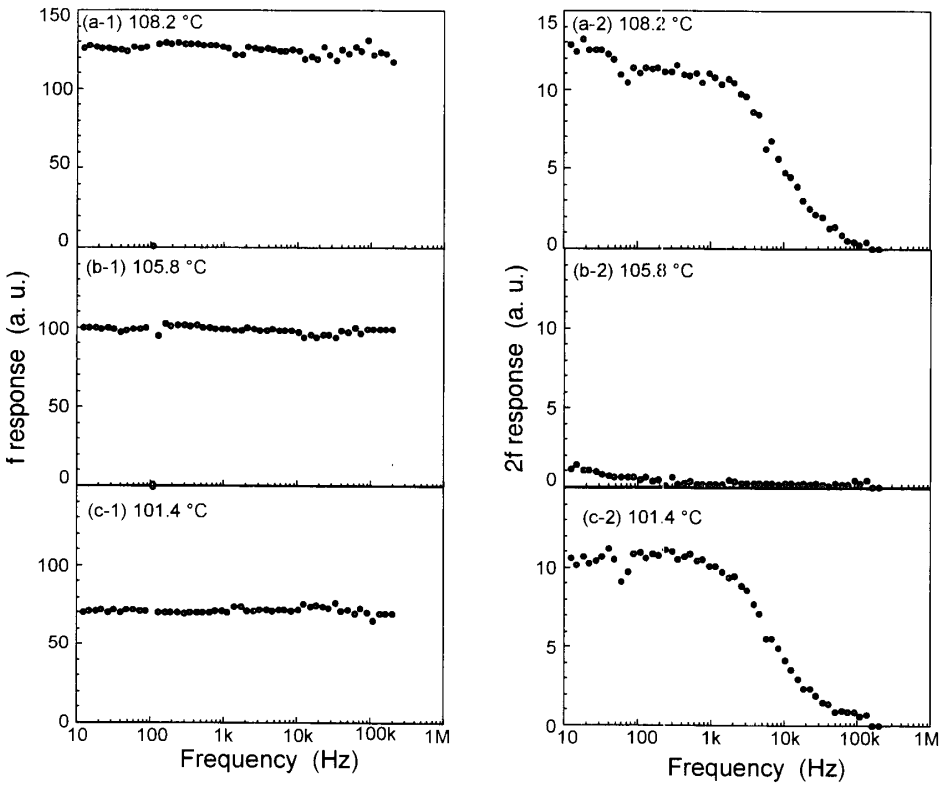

Fig. 4 Frequency dependence of optical signal of f and $2f$ response to an applied field of frequency f. A relaxation at 5 kHz was observed in both (a-2) and (c-2).

ing paragraph.

In order to discuss the details of the fluctuation modes in the antiferroelectric SmC_A^* phase, typical frequency dependences of the signals of f and $2f$ response are plotted in Fig. 4. Figures 4(a-1), 4(a-2), 4(c-1) and 4(c-2) show the frequency dispersions of f and $2f$ response at the temperatures indicated by arrows (a) and (c) in Fig. 3, respectively. Just below the SmA-SmC_A^* phase transition temperature, though no relaxation is recognized in an f response curve (Fig. 4(a-1)), a relaxation is observed in the $2f$ one at about 5 kHz (Fig. 4(a-2)). The relaxation of the $2f$ signal is attributed to the antiferroelectic Goldstone mode of the SmC_A^* phase, since the same relaxation behavior of the Goldstone mode has already been reported in another antiferroelectric liquid crystal, MHPOBC [13].

Figures 4(c-1) and 4(c-2) were measured below the turning point indicated by arrow (b) in Fig. 3. We easily notice that the relaxation behavior is almost the same as that of Fig. 4(a-1) and 4(a-2). Accordingly, the antilerroelectric Goldstone mode is also assigned as the cause of the relaxation of the $2f$ response in Fig. 4(c-2). Furthermore, the signal strength of the f response in Fig. 4(c-1) is smaller than that in Fig. 4(a-1), because the soft mode contribution decreases with decreasing temperature.

Figures 4(b-1) and 4(b-2) show the dispersion curves of the optical response at the temperature indicated by arrow (b) in Fig. 3, where the intensity of the $2f$ signal due to the antiferroelectric Goldstone mode vanishes. In fact, the amplitude of the $2f$ response is very small in the measured frequency range of Fig. 4(b-2).

IV. DISCUSSION

Why does the $2f$ response due to the antiferroelectric Goldstone mode vanish? In order to answer this question, we would like to discuss both the dielectric and optical properties of the SmC_A^* phase. Firstly, we would like to consider the experimental results from the view of dielectric anisotropy of the SmC_A^* phase. In order to explain the curious behavior of the Goldstone mode in an antiferroelectric liquid crystal, TFMHPOBC, let us take it for granted that the dielectric tensor of SmC_A^* is represented by the local electric permittivity ellipsoid of a single layer in the antiferroelectric molecular ordering shown in Figure 5. As a matter of course, a tensor of the local electric permittivity ellipsoid has three independent components in the SmC_A^* phase, because the hindered rotational motion about the molecular long axis makes the ellipsoid biaxial [20,21]. Let us denote the principal values of the local electric permittivity ellipsoid, ε_1, ε_2 and ε_3, where ε_1 denotes the electric permittivity in the tilt plane, perpendicular to the molecular long axis, ε_2 denotes the electric permittivity in the direction perpendicular to the molecular long axis

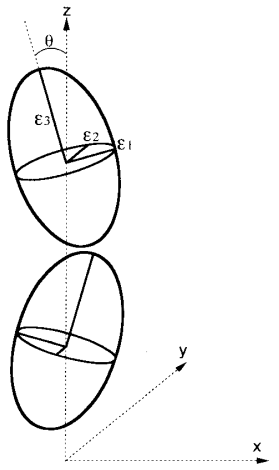

Fig. 5 Schematic illustration of the local single layer electric permittivity ellipsoid in antiferroelectric molecular ordering, where ε_1, ε_2 and ε_3 are eigenvalues of the ellipsoid, and θ is molecular tilt angle. The tilt plane corresponds to x-z plane.

and to the tilt plane, whereas ε_3 expresses the electric permittivity along the molecular long axis. We easily obtain the following dielectric tensor of SmC$_A$* in the coordinates in which the x axis lies in the tilt plane and the z axis is perpendicular to the smectic layers.

$$\varepsilon=\begin{pmatrix}\varepsilon_x & 0 & 0\\ 0 & \varepsilon_y & 0\\ 0 & 0 & \varepsilon_z\end{pmatrix}$$
$$=\begin{pmatrix}1/((\cos^2\theta)/\varepsilon_1+(\sin^2\theta)/\varepsilon_3) & 0 & 0\\ 0 & \varepsilon_2 & \\ 0 & 0 & 1/((\sin^2\theta)/\varepsilon_1+(\cos^2\theta)/\varepsilon_3)\end{pmatrix}, \quad (2)$$

where θ is the molecular tilt angle.

The components of the dielectric tensor, namely ε_x and ε_z are expected to greatly depend on temperature just below the SmA-SmC$_A$* phase transition, because the tilt angle increases with decreasing temperature[22]. Namely, the dielectric biaxiality is dependent on temperature just below the transition. It should be noted that the dielectric tensor of SmC$_A$* describes a uniaxial crystal at a certain tilt angle satisfying the following equation.

$$\varepsilon_2=1/((\cos^2\theta)/\varepsilon_1+(\sin^2\theta)/\varepsilon_3). \quad (3)$$

The $2f$ response of helix distortion due to the dielectric anisotropy cannot be excited by an electric field at the temperature where the dielectric tensor is uniaxial, so that the signal of the antiferroelectric Goldstone mode vanishes in the electrooptic measurements.

Let us examine whether the above interpretation is actually applicable to the material used. For the sake of further discussion, we would like to estimate the value of the components of the dielectric tensor in the SmC$_A$* phase of TFMHPOBC. ε_3 is likely to be the largest in three components, because the dielectric anisotropy of the non-tilted SmA phase is positive in TFMHPOBC [7]. In addition, ε_2 parallel to the local polarization seems to be larger than ε_1, as suggested by dielectric measurements ever made [23]. Accordingly, the following solution of eq. (3), namely

$$\theta_{uni}=\sin^{-1}\sqrt{\frac{(\varepsilon_3(\varepsilon_2-\varepsilon_1))}{(\varepsilon_2(\varepsilon_3-\varepsilon_1))}}, \quad (4)$$

is physically acceptable, because the part in the square root is positive. Thus we see that the dielectric tensor of SmC$_A$* really describes a uniaxial crystal at the tilt angle, θ_{uni}.

We illustrate the schematic models of the helix distortion caused by an electric field in Fig. 6, in order to imagine the behavior of the antiferroelectric Goldstone mode above and below the temperatre where the ellipsoid described by eq. (2) becomes uniaxial. We may

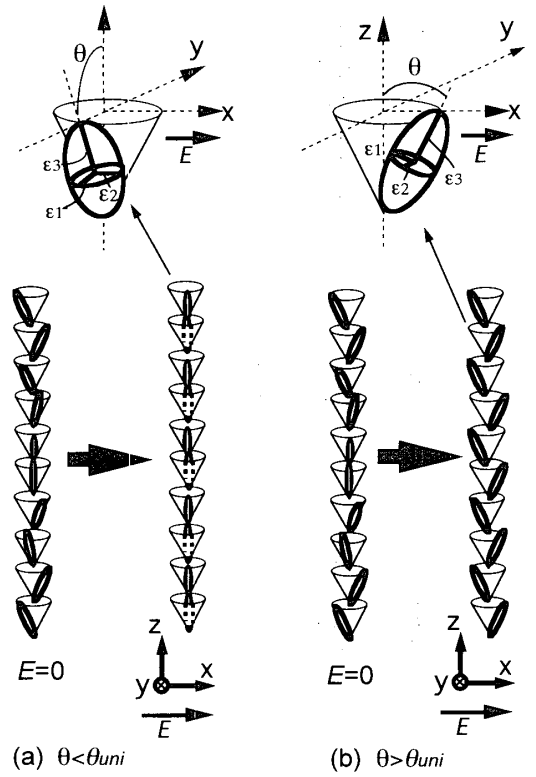

Fig. 6 Two schematic models of helix distortion due to the antiferroelectric Goldstone mode under an electric field, E. Note that tilt plane is perpendicular to an electric field applied in (a), which is observed just below SmA-SmC$_A$* phase transition temperature.

easily suppose that there exist two types of the helix distortion processes under a field. Figure 6(a) shows an unwinding process in the condition that tilt angle is smaller than θ_{uni}. The direction of an electric field is perpendicular to the tilt plane, because the dielectric constant perpendicular to the tilt plane (ε_x), is larger than that parallel to the tilt plane (ε_y). The distortion seems to occur above the temperature where the ellipsoid becomes uniaxial. In the other process, the field direction is parallel to the tilt plane as illustrated in Fig. 6(b). This type of the helix distortion is likely observed in lower temperature range where the tilt angle is larger than θ_{uni}.

We have seemingly succeeded in clariaying the experimental results by the use of the local electric permittivity ellipsoid. The above explanation, however, may be incorrect, because the experimental results can be also explained from the view of optical anisotropy. For further discussion, we would like to consider the change of the transmitted light intensity (ΔI) carefully. Let us examine eq. (1) again. It is worth while to notice that the optical anisotropy, namely the birefringence Δn in eq. (1) is dependent on temperature just below the SmA-SmC_A* phase transition. We can put

$$\phi = \phi_0 + \delta\phi, \qquad (5.1)$$

$$\Delta n = \Delta n_0 + \delta(\Delta n), \qquad (5.2)$$

where ϕ_0 and Δn_0 are equilibrium values in the absence of a field, and $\delta\phi$ and $\delta(\Delta n)$ are electrically-induced parts. Substituting the eqs. (5) into eq. (1), we obtain the $2f$ contribution of the antiferroelectric modes to the change of the transmitted light intensity, $\Delta I(2f)$: [24]

$$\Delta I(2f)/I_0 = (\pi d/\lambda)\sin^2(2\phi_0)\sin(2\pi d\Delta n_0/\lambda)\cdot\delta\phi. \qquad (6)$$

The temperature dependence of the Δn_0 could be responsible for the vanishing of $\Delta I(2f)$, when the $2d\Delta n_0$ is an integer multiple of λ. This may be achieved at one peculiar temperature in the SmC_A* phase.

We have discussed the experimental results by the use of the local electric permittivity ellipsoid whose principal values, ε_1, ε_2 and ε_3, are fixed. But the details still remain to be worked out in the future, because the principal values as well as the tilt angle depend on temperature. Numerical quantities of the principal values of the local electric permittivity ellipsoid in chiral smectic phases are deeply concerned in the hindered rotational motion, which is just the frontier problem [25-31]. For the purpose of the further discussion, we have been investigating full details of the optical and dielectric properties near the phase transition point in some antiferroelectric and ferroelectric liquid crystals.

V. CONCLUSION

We have measured the temperature and frequency dependences of the optical response due to the Goldstone and soft modes in an antiferroelectric liquid crystal, TFMHPOBC. We found that the amplitude of the optical signal due to the antiferroelectric Goldstone mode vanishes at a certain temperature in the SmC_A* phase. We tried to explain the curious behavior in the view of both the dielectric and optical properties. Furthermore, two types of helix distortion models concerning the antiferroelecric Goldstone mode were speculated on the basis of the electrooptic measurements.

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