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Critical anomalies in thermal diffusivity of liquid-crystalline terephthal-bis-(4-*n*-butylaniline)

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A temperature wave method has been applied to observe the thermal diffusivity through the isotropic (Iso)–nematic (N)–smectic Sm-*A*–Sm-*C*–Sm-*B*–crystals VI-VII-VIII phase transitions of terephthal-bis-(4-*n*-butylaniline) (TBBA). Critical anomalies have been found in the N–Sm-*A* and Sm-*C*–Sm-*B* phase transitions as diplike shaped, consistent with the predictions based on the dissipative couplings between the order parameter and the conserved free-energy density. Singular points with a gap have been observed at the Sm-*B*–crystal VI, crystals VI-VII, and crystals VII-VIII phase transitions, which show polymorphic behaviors on heating and cooling. The second-order Sm-*A*–Sm-*C* phase transition emerged as a singular temperature dependence. In all the phases thermal diffusivity decreases with increasing temperature except for Sm-*C*, where thermal diffusivity increases with increasing temperature. The origin of the anomaly in the thermal diffusivity in Sm-*C* is discussed based on the parametric analysis of dynamic critical behavior in the Sm-*A*–Sm-*C* phase transitions together with the tilt angle change obtained by use of simultaneous measurements of x-ray diffraction and differential scanning calorimetry.

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I. INTRODUCTION

Critical behaviors relevant to various phase transitions are one of the major physical problems. Liquid crystals exhibit a wide variety of phases, providing good examples for studying the critical phenomena associated with phase transitions.

With growing importance of the thermal transport properties in electronic devices, suitable experimental techniques with high accuracy over phase transitions have been required. Thermal diffusivity is one of the most important physical parameters in studying critical phenomena. Unfortunately, however, only a few groups have reported thermal diffusivity [1–5]. Moreover, it is known that thermal diffusivity α and thermal conductivity λ are anisotropic in the smectic and the nematic phases of liquid crystals [6,7]. In the smectic *A* (Sm-*A*)–nematic (N) phase transition, however, the critical behavior of λ was reported to be isotropic [2]. According to a simple model [5] for the thermal diffusivity of an extended mean-field-like Sm-*A*–smectic C (Sm-*C*) transition, the critical behavior is isotropic. Hence, it might be interesting to investigate the anisotropy in the critical phenomenon of thermal diffusivity more precisely. For this purpose, we need to develop a technique to measure thermal diffusivity with high accuracy. In this paper, we report the precise measurements of thermal diffusivity over various phase transitions in a standard liquid crystalline compound, terephthal-bis-(4-n-butylaniline) (TBBA), though we used nonaligned samples. In the previous studies of thermal diffusivity of liquid crystals the Sm-N and N-isotropic (Iso) phase transitions have been measured [2,3,8–13] and discussed from the viewpoint of mean-field theory. However, the thermal diffusivity in the Sm-*B*–Sm-*C*–Sm-*A* transitions and the polymorphic behavior of the crystal phase have not been precisely measured. In this paper, particular attention has been paid to the thermal diffusivity in the phase transitions among smectic phases in view of critical behavior and structure analysis.

II. EXPERIMENTAL DETAILS

The temperature wave method [14,15] was adopted for high sensitivity thermal diffusivity measurements. The sensors and heaters were sputtered for reliable implementation of the temperature wave analysis (TWA), which relies on the measurement of the phase delay, $\Delta\theta$, using a lock-in technique,

$$\Delta\theta = -\sqrt{\frac{\omega}{2\alpha}}\delta - \beta_0, \tag{1}$$

where α is the thermal diffusivity, ω is the frequency of the temperature wave, δ is the thickness of the sample, and β_0 is the phase accounting for actual experimental conditions and background noise. Thermal diffusivity at a constant temperature was determined from a slope in the plot of $\sqrt{\omega}$ vs $\Delta\theta$ in the frequency scan measurement. In order to observe the change of thermal diffusivity during phase transitions, a sinusoidal temperature wave of 18 Hz was input under the temperature scan at a rate of 0.3 K/min, considering the thermally thick condition of the one-dimensional heat flow. The sputtered sensor and heater were chemically stable with a low electric resistivity and good thermal conductivity: 315 W/mK for Au and 71 W/mK for Pt at 300 K. Typically a sensor of 100 Ω was used which did not add up noise to measurements compared with a thermal noise, $V = \sqrt{4kTR\Delta f}$. Here k is the Boltzmann constant, R is the electrical resistance, and Δf is the bandwidth, in hertz, over which the noise is measured. A heat source for generating a temperature wave was a 300-nm-thick layer of Au with an area size of $1 \times 5\ \mathrm{mm}^2$ and was larger than the sensor Pt $0.5 \times 1\ \mathrm{mm}^2$, which assured one-dimensional heat flow. It has an electrical resistance of 50 Ω. The modulated thermal power was chosen to satisfy a good signal-to-noise ratio required for detection of thermal diffusivity change on the order less than 1–3%. The specimens were prepared in the nonaligned situation.

The x-ray diffractometer RINT-Ultima-TTR III (Rigaku) [16] coupled with a heat-flux-type differential scanning calorimetry (DSC) was used for simultaneous measurements of the layer spacings and phase transition temperatures. The x-ray source was 0.154-nm CuKα monochromatized with a Kβ filter, a high-powered rotating anode-type x-ray generator. Utilizing the silicon strip detector (SSD) D/teX Ultra, a scanning rate of 40.0 °/min at a 0.007 °/step was operated in the range of 2.6–27.0 °/2θ. The temperature range was from 250 °C to 40 °C at a constant cooling or heating rate. The cyclic fluctuation in the DSC signal by use of x-ray high power was eliminated using fast Fourier transform signal analysis. Specimen holders were a couple of square-shaped aluminum containers of 7 × 7 mm^2 in area size and 0.25 mm in depth for a specimen and reference materials which were put in a relatively thick-walled furnace made of silver. On both sides of the furnace, two-small x-ray windows were opened, which were covered with a thin aluminum foil to minimize convection and heat loss. Specific heat C_p was measured with DSC (204F1 Phoenix/μ–Sensor, NETZSCH) by using a Pt/Rh pan with a lid, in which a specimen having a weight of 9.6 mg was sealed. The nitrogen gas flow rate was 40 ml/min, and sapphire, indium, and tin were used for the calibration.

III. RESULTS AND DISCUSSION

Thermal diffusivity α of TBBA in the Sm-*A*–Sm-*C*–Sm-*B*–crystals (VI)-VII-VIII [5,17–30] phase sequence on cooling is shown in Fig. 1(a). On heating, the crystal (III)–Sm-*B*–Sm-*C*–Sm-*A*–N phase sequence is shown in Fig. 1(b). The specific heat C_p and the layer spacing d are plotted as a function of temperature. All of these values, α, C_p, and d, exhibit characteristic anomalies near the phase transition temperatures. The phase transition temperatures determined from α, C_p, and d are summarized in Table I. Note that the transition temperatures determined by XRD-DSC, DSC, and TWA well agree with each other.

The phase transition temperatures obtained agree with the data reported by Das [18], Blinc [24], Docet [29], and Kumar

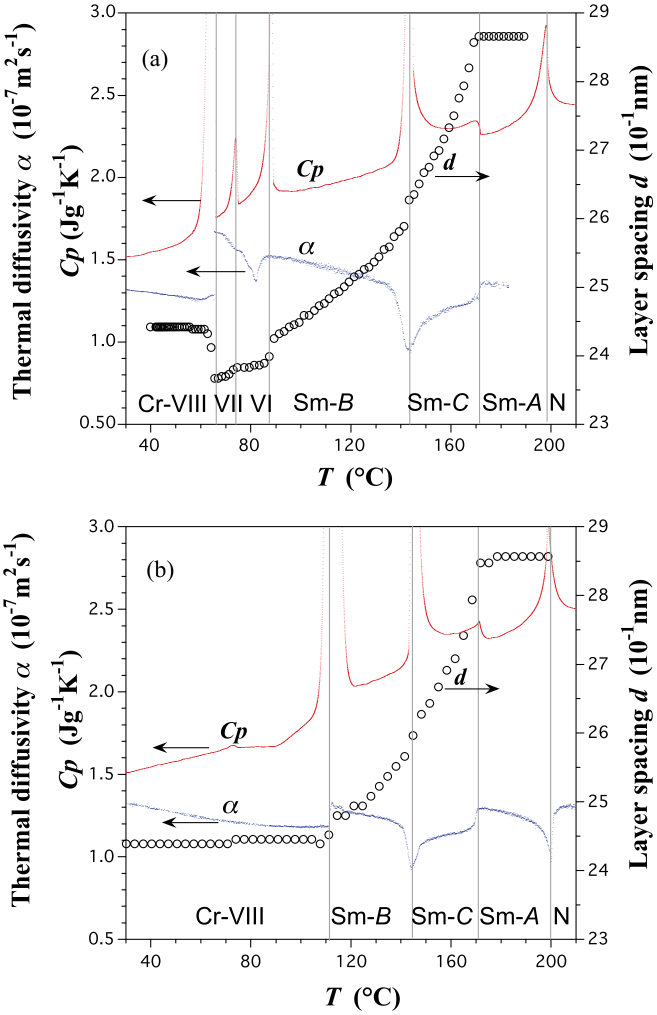

FIG. 1. (Color online) Thermal diffusivity of TBBA measured with an 18-Hz sinusoidal temperature wave, specific heat C_p, and a layer spacing calculated from main Bragg peak on (a) cooling and (b) heating. The cooling and heating rates in these three measurements are 0.3 K/min, 5 K/min, and 3 K/min, respectively.

TABLE I. Phase transition temperatures of TBBA in the smectic and crystal phases with different methods of heating and cooling.

Heating	TWA[a]	DSC[b]	XRD-DSC	DSC[c]	AC[d]	Cooling	TWA[a]	DSC	XRD-DSC	DSC[c]
—						Cr.VII–Cr.VIII	65.3	65.3[e]	65.3[f]	
—						Cr.VI–Cr.VII	73.1	73.9[e]	73.2[f]	71.1
—						—	82.1			
—						Sm-*B*–Cr.VI	87.1	88.3[e]	87.4[f]	85.8
Cr.VIII–Sm-*B*	112.5	112.8	111.1[f]			—				
Sm-*B*–Sm-*C*	144.2	144.7	144.0[g]	144.2	144.0	Sm-*C*–Sm-*B*	143.9	145.0[b]	143.9[g]	
Sm-*C*–Sm-*A*	170.7	171.4	170.6[g]	172.2	172.0	Sm-*A*–Sm-*C*	171.6	171.9[b]	171.9[g]	
Sm-*A*–N	200.0	198.4	199.6[g]	199.5	200.0	N–Sm-*A*		199.0[b]		
N-I		235.2		235.3	232.0	I-N		233.8[e]		

[a] 18 Hz, 0.3 K/min.

[b] 1 K/min.

[c] Cited from Ref. 28.

[d] Cited from Ref. 17, 31.25 mHz, 70 mK/h.

[e] 5 K/min.

[f] 3 K/min.

[g] 1 K/min.

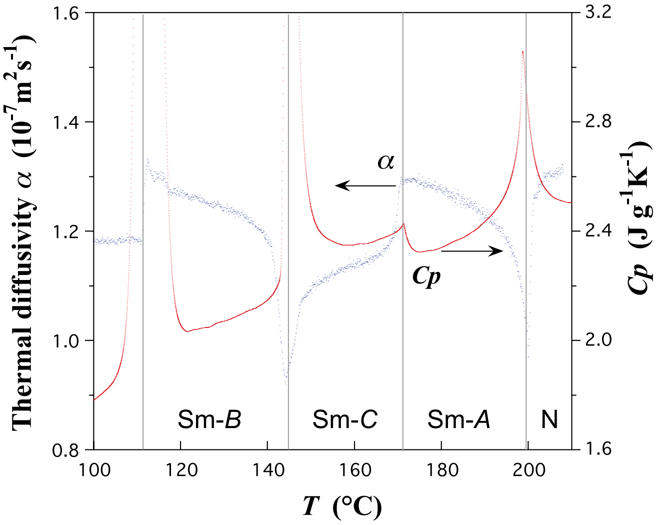

FIG. 2. (Color online) Plot of α and C_p in the liquid crystalline temperature range. The data are extracted from Fig. 1(b).

[30]. The polymorphic behavior in the crystal phase was found and the crystal phases VI and VII were observed only on cooling. Figure 2 is the data extracted from Fig. 1(b) for the plot of α and C_p in the liquid crystalline temperature range. As previously reported in octylcyanobipheny (8CB) [2], a diplike anomaly in thermal diffusivity was observed in the Sm-A–N phase transition as a consequence of the λ-type anomaly in C_p. Far from the transition points, thermal diffusivity decreases and C_p increases with increasing temperature in the Sm-B and Sm-A phases, whereas in the Sm-C phase both increase with increasing temperature and asymptotically increase up to the Sm-C–Sm-A transition. Das [18] reported the λ-type anomaly of C_p in the Sm-A–Sm-C phase transition of TBBA by using an ac calorimetry technique.

In order to investigate the origin of the characteristic change of thermal diffusivity in the Sm-C phase, the tilt angle $\theta(T)$ was determined using the layer spacing $d(T)$ [see Eq. (2)]. Figures 3(a) and 3(b) show the temperature dependence of the tilt angle in the Sm-A–Sm-C–Sm-B phase sequence measured at a rate of 1 K/min on cooling and heating, respectively. Thermal diffusivity measured at 18 Hz, 0.3 K/min is also replotted. The tilt angle increases rapidly on the transition from Sm-A to Sm-C and exhibits a finite jump at the Sm-C–Sm-B transition. The fitting function

$$d(T) = d_{AC}\cos\theta(T) = d_{AC}\cos[a(b-T)^{\beta}] \qquad (2)$$

is used to fit the data points in the Sm-C phase, where d_{AC} is the layer thickness in the Sm-A phase near the Sm-A–Sm-C transition. The experimental result is fitted to Eq. (2) in the temperature range 160.0 °C–170.7 °C as shown in Fig. 4 and the best fit gives $\beta = 0.356 \pm 0.003$, $a = 0.136 \pm 0.001$, $b = 170.5 \pm 0.02$, and $d_{AC} = 29.1$ Å.

Thermal diffusivity decreases with decreasing temperature in the Sm-C phase; i.e., rapid decreases at Sm-A–Sm-C and Sm-C–Sm-B phase transitions and a gradual decrease in between. In the second-order transition of Sm-A–Sm-C, where the tilt angle rapidly increases, the decrease of thermal diffusivity is most prominent, suggesting the effect of layer shrinkage on thermal diffusivity. In other words, the layer shrinkage introduces thermal mismatch at the interface of the layers. The validity of this idea can be examined by using so-called de Vries–type compounds, which do not show layer shrinkage. The measurements of the anisotropy in thermal diffusivity may also give important information.

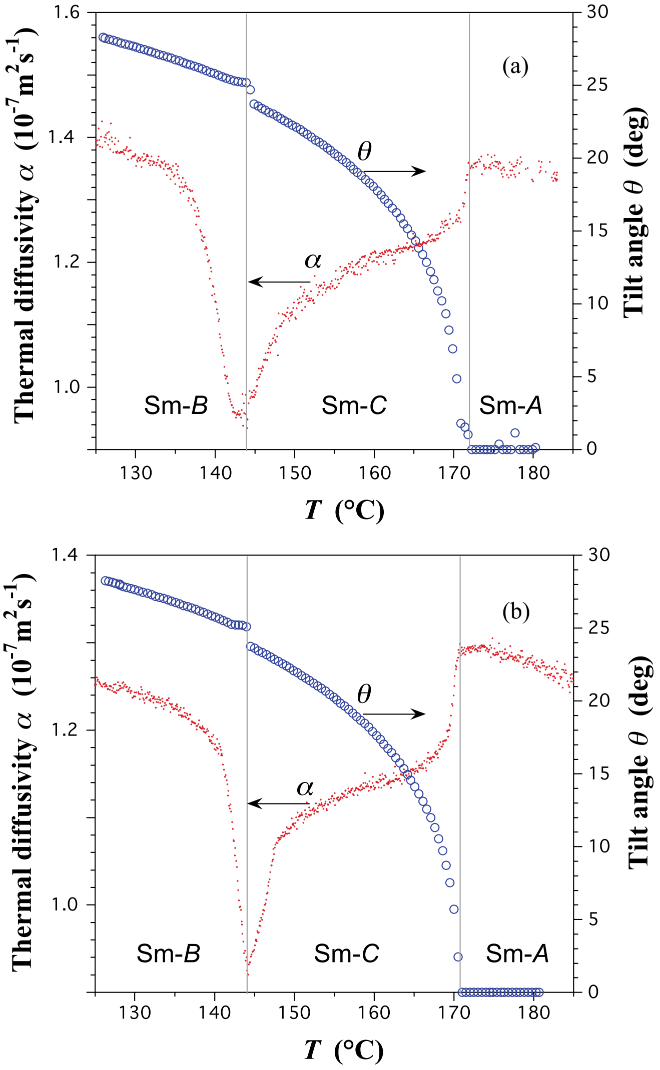

FIG. 3. (Color online) Layer spacing and thermal diffusivity of the smectic phases of TBBA on (a) cooling and (b) heating. The layer spacing is obtained from the main Bragg peak under a cooling rate of 1 K/min. Thermal diffusivity is measured with 18 Hz at a rate of 0.3 K/min.

The temperature dependence of the heat capacity anomaly is derived from the mean-field free energy for the Sm-A–Sm-C transition as [31,32]

$$C_p = C_0 + AT(T_m - T)^{-1/2}, \quad T < T_c, \qquad (3)$$

where C_0 is the background heat capacity obtained from G_0, $A = (a/T_c)^{3/2}/2(3c)^{1/2}$, $T_m = T_c(1 + t_0/3)$, and $t_0 = b^2/ac$. The constants a, b, and c are the expansion coefficients of the free energy $G = G_0 + at\theta^2 + b\theta^4 + c\theta^6$ and $t = (T - T_c)/T_c$. Das *et al.* [18] applied this equation to analyze the specific heat capacity of TBBA near the Sm-A–Sm-C

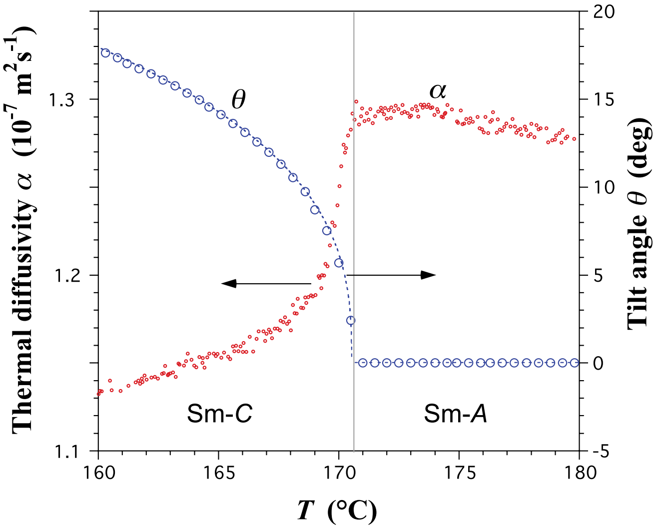

FIG. 4. (Color online) Thermal diffusivity and tilt angle of Sm-C of TBBA on heating. The tilt angle is calculated from the data in Fig. 2 and fitted with Eq. (2).

transition. Hobbie *et al.* [5] used an approximation from a hydrodynamic theory of smectic liquid crystals [33] and obtained

$$\alpha \approx C_0(A^{\pm}|t|^{-1/2} + B)^{-1}. \tag{4}$$

The thermal diffusivity near the Sm-A–Sm-C transition of racemic 4-(3-methyl-2-chlorobutanyloxy)-4-heptyloxybiphenyl (A7) shows a mean-field tricritical point and is fitted by Eq. (4) [5]. Since the hydrodynamic theory predicts that the thermal diffusivity goes to zero at T_c [5], the data in Fig. 5(a) is inconsistent with the theory. If Eq. (4) was applied, the parameters obtained by the least-mean-squares fitting give a contradictory negative value of $A^- = -0.000426$, when $T_c = 170.5\,^\circ\mathrm{C}$, $B = 2.70$, and $C_0 = 3.03 \times 10^{-07}$ in the fitting range of t from -0.015 to -0.00025.

On the other hand, in the first-order transition of Sm-C–Sm-B, where the latent heat is observed and the layer spacing d changes discontinuously, thermal diffusivity rapidly decreases near the Sm-C–Sm-B transition, although the variation is more gradual than that in the Sm-A–Sm-C transition and the rate of change does not correspond to that of layer spacing d. In contrast to the discontinuous jump of d at a phase transition temperature, the diplike anomaly in the thermal diffusivity emerges in the wide temperature range. This process is attributed to the change of the symmetry from C_{2h} of Sm-C to the hexagonal C_6 of Sm-B. The results suggest that the disordering of the molecular orientation during the Sm-C–Sm-B transition dissipates the thermal diffusion and reduces the thermal diffusivity.

The critical behavior of thermal diffusivity, thermal conductivity, and specific heat at the Sm-A–N transition of octylcyanobiphebyl (8CB) was studied by Marinelli *et al.* [2,3]. They concluded that the critical behavior of thermal diffusivity was isotropic in spite of their absolute values significantly differing in the planar and vertical alignments.

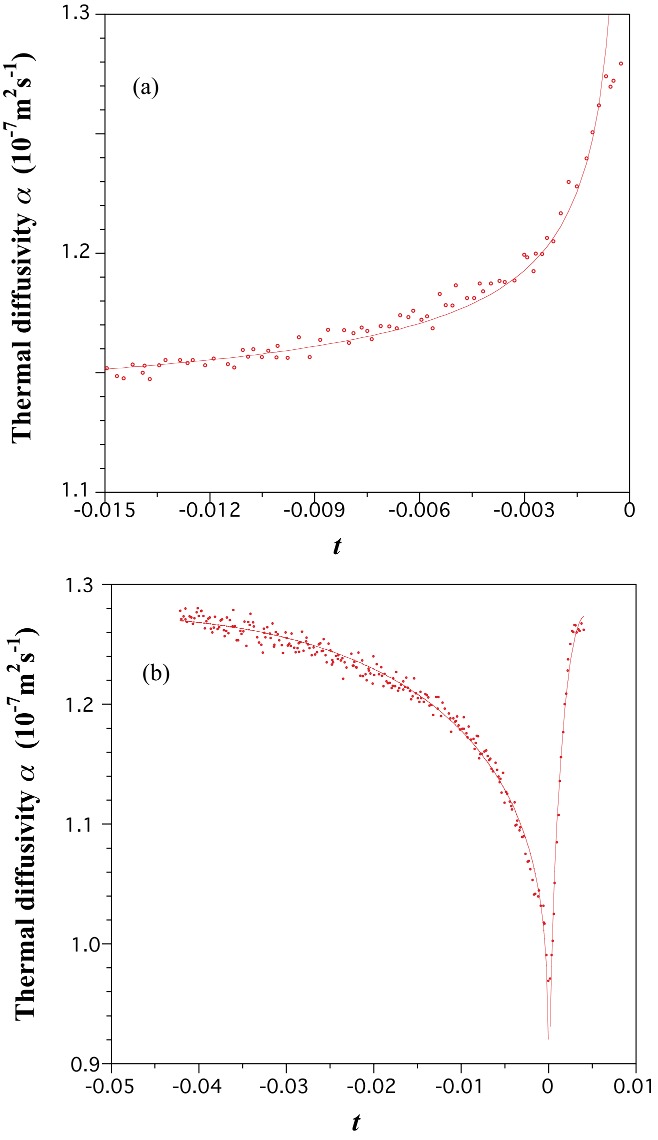

FIG. 5. (Color online) Measured thermal diffusivity (dotted) as a function of $t[t = (T - T_c)/T_c$; T, temperature in K; T_c, phase transition temperature] and calculated fitted values (line) with (a) Eq. (4) near the Sm-C–Sm-A transition and (b) Eq. (5) near the N–Sm-A transition of TBBA.

The fitting expression has been derived as

$$\alpha = \frac{D_0}{1 + W(T - T_c) + U^{\pm}|T - T_c|^{-b}(1 + F^{\pm}|T - T_c|^{0.5})}, \tag{5}$$

which originates from the assumption of a nondivergent behavior of thermal conductivity. Figure 5(b) shows the fit results of thermal diffusivity of TBBA in the Sm-A–N phase transition in the fitting range from 0.00004 to 0.004 and from -0.04 to -0.0001. The critical exponent $b = -0.023$ is in good agreement with the ones reported in Refs. [2,3,34,35]. The parameters obtained by the best fit of Fig. 5(b) to Eq. (5) are shown in Table II.

In liquid crystals, since the order parameter fluctuations are strong thermal modes of the system, the thermal diffusion mode is coupled with the order parameter mode [2,3]. The

TABLE II. Parameters determined by fitting data to Eq. (5) in the Sm-*A*–N phase transition.

Parameter	b	U^-, U^+	T_c (K)	$10^{-8}D_0$ (m^2/s)	W	F^-, F^+	$10^{-18}\chi^2$
t^-	−0.023	−0.589	443.65	4.26	−0.00263	0.0307	0.477
t^+	−0.023	−0.523	443.65	4.20	0.0876	0.418	2.01

hydrodynamics is based on a free energy function in which an isotropic dissipative coupling of the order parameter with the conserved energy density has been included. In this model, a dynamic quantity such as the thermal diffusivity goes to zero at T_c, while the thermal conductivity remains constant over the transition temperature region. By contrast, in the case of superfluid of He, a model with a nondissipative coupling of the nonconserved energy density and the order parameter in the free energy function has been proposed to explain the divergence of the thermal conductivity at T_c [36]. In the previous studies of thermal diffusivity of liquid crystals, only a few reports are known with limited experimental conditions in the Sm-*C*–Sm-*A* phase transition. The thermal diffusivity over Sm-*A*–N transition is understood by use of hydrodynamic theory. However, the thermal diffusivity over Sm-*C*–Sm-*A* is not well explained, since the thermal diffusivity goes up, not to zero, unlike the prediction by the hydrodynamic theory.

IV. CONCLUSION

The temperature wave method was applied to measure the thermal diffusivity of TBBA with the phase sequence of nematic (N)–Sm-*A*–Sm-*C*–Sm-*B*–crystals VI-VII-VIII. The phase transition temperature in thermal diffusivity agrees with the results measured with DSC, XRD-DSC, and the various literature values. The critical behavior in the thermal diffusivity was obtained in the N–Sm-*A* and Sm-*A*–Sm-*C* transitions and found to show different behaviors. The thermal diffusivity anomaly in the N–Sm-*A* transition is explained by the mean-field type and its diplike shape is consistent with hydrodynamic theory, whereas the asymptotical increase of the thermal diffusivity close to the transition temperature of Sm-*A*–Sm-*C* is inconsistent. The critical factor obtained together with the tilt angle or the layer spacing in the Sm-*C* phase suggests a second-order phase transition.

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