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Experimental Evidence for a Hyperscaling Relation at a Nematic to Smectic A Phase Transition

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A hyperscaling relation $\nu_{\parallel} + 2\nu_{\perp} = 2 - \alpha$ is examined for the nematic to smectic A transition of 4-octyloxy-4′-cyanobiphenyl (8OCB) and 4-octyl-4′-cyanobiphenyl (8CB). From the heat capacity results, $2-\alpha$ is analyzed to be 1.84 ± 0.03 for 8OCB and 1.75 ± 0.02 for 8CB. On the other hand $\nu_{\parallel} + 2\nu_{\perp}$ is calculated from the results reported by X-ray experiments to be 1.87 ± 0.12 for 8OCB and 1.69 ± 0.11 for 8CB. From the above coincidences the hyperscaling relation is found to be applicable to the nematic to smectic A transition.

1 INTRODUCTION

Since de Gennes' suggestion[1,2] that the phase transition between a nematic phase and a smectic A phase, hereafter abbreviated as NA transition, might be analogous to the superfluid transition of ^{4}He, much theoretical and experimental effort has been devoted to a study of this problem. Halperin and Lubensky[3] have shown that the fluctuation of the director results in a first order phase transition, but it is very close to a second order phase transition. Furthermore, they have pointed out that the effective critical exponents should be the same as for the superfluid transition.[3]

The critical exponents obtained experimentally, however, do not always agree with those of the superfluid transition, i.e., the exponents of a three dimensional XY system. Among these facts, it is quite striking that the critical exponents of the correlation length have been reported to vary with direction.[4,5] In 4-cyanobenzylidene-4′-*n*-octyloxyaniline (CBOOA), $\nu_{\parallel} = 0.70$

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$\pm$ 0.04 and $\nu_\perp = 0.62 \pm 0.05$, in 4-octyloxy-4′-cyanobiphenyl (8OCB), $\nu_\parallel = 0.71 \pm 0.04$ and $\nu_\perp = 0.58 \pm 0.04$, and in 4-octyl-4′-cyanobiphenyl (8CB), $\nu_\parallel = 0.67 \pm 0.03$ and $\nu_\perp = 0.51 \pm 0.04$, where $\parallel$ and $\perp$ denote the direction parallel and perpendicular to the director of nematic ordering, respectively. For such a case, a hyperscaling relation $\nu_\parallel + 2\nu_\perp = 2 - \alpha$ has been proposed by Lubensky and Chen.[5] In this connection, it is of interest to examine the critical exponents α, α' of the specific heat capacity for CBOOA, 8OCB and 8CB. The specific heat capacity of CBOOA has been measured by Djurek *et al.*[6] and the critical exponents α and α' have been obtained as 0.16 ± 0.01 and 0.14 ± 0.02, respectively. It is clearly seen that α and α' substantially deviate from zero (logarithmic divergence), but, satisfy a scaling relation $\alpha = \alpha'$. For 8OCB there is conflicting evidence concerning the critical exponents of the specific heat capacity. Johnson *et al.*[7] have reported them to be consistent with a logarithmic divergence, which is expected in a three dimensional XY system. On the other hand, recent specific heat measurements for 8OCB carried out by Garland *et al.*[8] agree with a power law divergence, with $\alpha = \alpha'$ in the range of $0.2 \sim 0.3$. We have performed independent experiments† using 8OCB and 8CB, in view of the establishment of the hyperscaling relation. Garland *et al.*[8] have also measured the specific heat capacity of 8CB and obtained a large positive α value in the $0.25 \sim 0.4$ range.

In this paper, the results of the analysis of the critical exponents α, α' for 8OCB and 8CB will be discussed and the examination of the hyperscaling relation will be made.

2 EXPERIMENTAL RESULTS AND ANALYSES

The specific heat capacity experiments were carried out by means of an a.c. calorimetry method. Liquid crystals were put between thin platinum plates and a chromel-alumel thermocouple was used for the a.c. temperature detection; this was attached to one of the surfaces of the platinum cell. The amplitude of the a.c. temperature was about 9 mK near the NA transition temperature (T_{NA}). The results were analysed by a least squares method fitting to the equations:

$$\begin{aligned} C_p &= At^{-\alpha} + B + Et \qquad T > T_{NA}, \\ C_p &= A'|t'|^{-\alpha'} + B' + E't' \qquad T < T_{NA}, \end{aligned} \tag{1}$$

where t and t' are $(T - T_{NA})/T_{NA}$ above and below T_{NA}, respectively. The

† Our experimental results were briefly reported at the Autumn Meeting of the Physical Society of Japan, Ehime, October 1979.

analysis was performed under the constraints $E = E'$ and $\alpha = \alpha'$. The latter condition is required from a scaling law.

8OCB assumes a crystalline phase below 327.0 K and a smectic A phase appears above this temperature. It forms a nematic phase at 338.8 K and successively transforms into an isotropic phase at 351.6 K. For 8CB, the sequence of the phases is the same as for 8OCB. A crystalline-smectic A transition occurs at 294.3 K, a transition to a nematic phase at 306.7 K, and, finally, a transition to the isotropic phase at 314.0 K. The present experiments were made in the temperature regions of 333 K to 347 K for 8OCB and of 298 K to 313 K for 8CB. The least squares fitting analysis was carried out for the results between $|t'|_{max}$ and $|t'|_{min}$ below T_{NA}, and between t_{min} and t_{max} above T_{NA}. Closer to 0 from $|t'|_{min}$ and t_{min}, the departures from Eq. (1) become significant and may be attributable to sample inhomogeneities. Then the results with smaller $|t'|$ and t should be discarded in the analysis. On the other hand, in the temperature regions beyond $|t'|_{max}$ and t_{max}, the normal part of Eq. (1) is no longer linear in t' and t, because a crystalline phase exists just below t'_{max} and an isotropic phase just above y_{max}. In Table I, t'_{max}, t'_{min}, t_{min}, t_{max}, T_{NA} and α are summarized for 8OCB. In Table II, the same quantities for 8CB are listed. As seen in Tables I and II, α is closer to a stable value as the temperature region used in the analysis becomes narrower. Therefore the present analysis is successful. Finally, we determined that $\alpha(=\alpha')$ is 0.16 ± 0.03 for 8OCB and 0.25 ± 0.02 for 8CB. The exponent for 8OCB is near to the smallest value, 0.2, obtained by Garland *et al.*[8] but clearly differs from the logarithmic divergence indicated by Johnson *et al.*[7] The exponent for 8CB corresponds to the smallest value, 0.25, in the region quoted by Garland *et al.*[8] The present results indicate that the critical exponents of the specific heat capacity at the NA transition are significantly different from logarithmic and depend on the substance. Details of the experimental results will be published elsewhere.

3 DISCUSSION

To examine the hyperscaling relation connecting $2 - \alpha$ with $\nu_{\parallel} + 2\nu_{\perp}$ which was derived from the experimental values, these values are listed in Table III for 8OCB and 8CB, together with the values for CBOOA.[4,6] Within experimental accuracy, the coincidences are good enough, except for CBOOA. In the case of CBOOA, a good quality sample is not easily available, in comparison with the other cases, and, for this reason, the coincidence may be rather poor.

In the superfluid transition, the critical exponent ν of the correlation length is 0.67. At the NA transition, $\nu_{\parallel}$ is larger than $\nu_{\perp}$, and the superfluid exponent

TABLE I

Temperature range used for the analysis of the data for 8OCB. The sixth and the seventh columns contain the calculated values of T_{NA} and $\alpha(=\alpha')$, respectively.

Experiment	t'_{max}	t'_{min}	t_{min}	t_{max}	T_{NA}(K)	α
A	-1.0×10^{-2}	-6.0×10^{-6}	6.0×10^{-6}	1.1×10^{-2}	339.432	0.169
B	-7.2×10^{-3}	-4.4×10^{-5}	4.4×10^{-5}	7.6×10^{-3}	339.430	0.174
C	-7.2×10^{-3}	-8.8×10^{-5}	8.8×10^{-5}	7.6×10^{-3}	339.433	0.158
D	-7.2×10^{-3}	-1.0×10^{-4}	1.0×10^{-4}	7.6×10^{-3}	339.440	0.154

TABLE II

Temperature range used for the analysis of the data for 8CB. The sixth and the seventh columns contain the calculated values of T_{NA} and $\alpha\,(=\alpha')$, respectively.

Experiment	t'_{max}	t'_{min}	t_{min}	t_{max}	T_{NA}(K)	α
A	-1.8×10^{-2}	0	0	1.4×10^{-2}	306.596	0.244
B	-1.5×10^{-2}	-4.9×10^{-5}	4.9×10^{-5}	1.4×10^{-2}	306.593	0.286
C	-6.5×10^{-3}	-4.9×10^{-5}	4.9×10^{-5}	7.8×10^{-3}	306.591	0.273
D	-6.5×10^{-3}	-8.2×10^{-5}	8.2×10^{-5}	7.8×10^{-3}	306.598	0.255
E	-5.2×10^{-3}	-1.3×10^{-4}	9.8×10^{-5}	4.6×10^{-3}	306.598	0.238
F	-5.2×10^{-3}	-1.6×10^{-4}	1.6×10^{-4}	4.6×10^{-3}	306.598	0.248

TABLE III

α, $v_{\parallel}$, $v_{\perp}$, $2-\alpha$, and $v_{\parallel} + 2v_{\perp}$ for CBOOA, 8OCB and 8CB.

Substance	α	$v_{\parallel}$[b]	$v_{\perp}$[b]	$2-\alpha$	$v_{\parallel} + 2v_{\perp}$
CBOOA	0.16 ± 0.01[a]	0.70 ± 0.04	0.62 ± 0.05	1.84 ± 0.01	1.94 ± 0.14
8OCB	0.16 ± 0.03	0.71 ± 0.04	0.58 ± 0.04	1.84 ± 0.03	1.87 ± 0.12
8CB	0.25 ± 0.02	0.67 ± 0.03	0.51 ± 0.04	1.75 ± 0.02	1.69 ± 0.11

[a] Ref. 6.
[b] Ref. 4.

lies between $\nu_{\parallel}$ and $\nu_{\perp}$. The critical exponents of the specific heat capacity at NA transitions are significantly different for different substances. Specific heat measurements at the NA transition have been made for pentylphenylthiol-octyloxybenzoate ($\bar{8}$S5), pentylphenylthiol-nonyloxybenzoate ($\bar{9}$S5) and pentylphenylthiol-decyloxybenzoate ($\overline{10}$S5).[9] Brisbin *et al.*[9] have reported that $\alpha\,(=\alpha')$ is 0.0 ± 0.02 (logarithmic divergence) for $\bar{8}$S5, 0.22 ± 0.03 for $\bar{9}$S5 and 0.45 ± 0.05 for $\overline{10}$S5. In the $\bar{n}$S5 homologous series, it has been concluded that there appears to be a tricritical point when $\bar{n} \gtrsim \bar{9}$ and, in consequence of a critical to tricritical crossover, the critical exponent of the specific heat capacity changes with $\bar{n}$. In the case of the $\bar{n}$S5 series, the value of α increases as the length of the molecule increases. On the contrary, α for 8CB is larger than that of 8OCB, in which the length of molecule is greater by an additional oxygen atom. Therefore the length of the molecule alone does not play an important role in altering the nature of the divergence of the specific heat capacity. At present, it is desirable that X-ray experiments be carried out on a number of substances, especially those in the $\bar{n}$S5 series. Such results for the $\bar{n}$S5 series would give another examination of the hyperscaling relation and strong evidence about the systematic change of the values of $\nu_{\parallel}$ and $\nu_{\perp}$.

The hyperscaling relation is derived from a length scale transformation. The correlation lengths are given by $\xi_{\parallel}$ and $\xi_{\perp}$ at the NA transition. The singular part of the free energy per unit volume is related to t as

$$F_s \propto t^{2-\alpha}. \tag{2}$$

The total free energy does not change under a length scale transformation. Therefore,

$$F_s \xi_{\parallel} \xi_{\perp}^2 = \text{const.} \tag{3}$$

From Eq. (3) one obtains

$$\nu_{\parallel} + 2\nu_{\perp} = 2 - \alpha. \tag{4}$$

In an actual substance, both correlation lengths become long as t decreases, and near T_{NA} grow with characteristic anisotropy when $\nu_{\parallel} > \nu_{\perp}$. In a sample of finite size, the growth of clusters is limited before the three dimensional order is built up, and this seems to be a feature of delicate first order transition as mentioned below. The latent heat, which gives a measure of first order nature, is 0.06 ± 0.02 cal/g for CBOOA, 0.10 ± 0.03 cal/g for 8OCB and 0.17 ± 0.05 cal/g for 8CB.[10] On the other hand $\nu_{\parallel} - \nu_{\perp}$ is calculated to be 0.08 ± 0.09 for CBOOA, 0.13 ± 0.08 for 8OCB and 0.16 ± 0.07 for 8CB from Ref. 4. As can be seen, there exists a strong correlation between the latent heat and the value of $\nu_{\parallel} - \nu_{\perp}$.

NOTE ADDED IN PROOF

In the paper by G. B. Kasting, K. J. Lushington, and C. W. Garland, *Phys. Rev.*, **B22**, 321 (1980), it was recorded that $\alpha = \alpha' = 0.25 \pm 0.05$ for 8OCB at 1 atm, 500 bar, and 1000 bar, and in that by G. B. Kasting, C. W. Garland, and K. J. Lushington, *J. Phys. (Paris)*, **41**, 1200 (1980), that $\alpha = \alpha' = 0.30 \pm 0.05$ for 8CB at 1 atm. Very recently on two different batches of 8OCB, similar experiments were carried out by J. D. LeGrange and J. M. Mochel, *Phys. Rev. Lett.*, **45**, 35 (1980). They obtained the results that on one sample (early batch) $\alpha = \alpha'$ is naught, inconsistent with Johnson's early measurements, while on the other sample (late sample), $\alpha = \alpha'$ is 0.25 ± 0.02, which agrees with Garland's measurements. Our results, on a sample which should be classified as a late batch, are closer to the latter results, but $\alpha = \alpha'$ is slightly smaller than in the other studies.

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