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OFFICE OF NAVAL RESEARCH

CONTRACT NO. N00014-86-K-0772

TECHNICAL REPORT NO. 16

Specific Heat Study of First Order Smectic A to Smectic B (Hexatic) Transitions in n-Alkyl-4'-n-Pentanoyloxy-Biphenyl-4-Carboxylates

by

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Prepared for Publication

in

Physical Review A

September 2, 1988

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Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

AD-A199 290

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION: Unclassified

1b RESTRICTIVE MARKINGS: None

2a SECURITY CLASSIFICATION AUTHORITY:

2b DECLASSIFICATION / DOWNGRADING SCHEDULE:

3 DISTRIBUTION / AVAILABILITY OF REPORT: Approved for Public Release, Distribution Unlimited

4 PERFORMING ORGANIZATION REPORT NUMBER(S): Technical Report No. 16

5 MONITORING ORGANIZATION REPORT NUMBER(S):

6a NAME OF PERFORMING ORGANIZATION: University of Connecticut

6b OFFICE SYMBOL (If applicable):

7a NAME OF MONITORING ORGANIZATION: Office of Naval Research

6c ADDRESS (City, State, and ZIP Code):
Storrs, CT 06268

7b ADDRESS (City, State, and ZIP Code):
800 North Quincy Avenue
Arlington, VA 22217

8a NAME OF FUNDING / SPONSORING ORGANIZATION:

8b OFFICE SYMBOL (If applicable): ONR /DARPA

9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N00014-86-K-0772

8c ADDRESS (City, State, and ZIP Code):
800 North Quincy Avenue
Arlington, VA 22217

10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)
SPECIFIC HEAT STUDY OF FIRST ORDER SMECTIC A TO SMECTIC B (HEXATIC) TRANSITIONS in n-Alkyl-4'-n-Pentanoylo xy-Biphenyl-4-Carboxylates (Unclassified)

12 PERSONAL AUTHOR(S)
R. Mahmood, M. Lewis, D. Johnson, and V. Surrendranath

13a TYPE OF REPORT: Interim, Technical

13b TIME COVERED: FROM ________ TO 09/02/88

14 DATE OF REPORT (Year, Month, Day): 1988-09-02

15 PAGE COUNT: 19

16 SUPPLEMENTARY NOTATION
Accepted for publication in Physical Review A
Research carried out at Kent State University (subcontractor) (LCPRC Publication No.LCPRC88-19)

17 COSATI CODES

FIELD	GROUP	SUB-GROUP

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

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20 DISTRIBUTION / AVAILABILITY OF ABSTRACT: ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21 ABSTRACT SECURITY CLASSIFICATION: Unclassified

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22c OFFICE SYMBOL: ONR

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

Accepted in Phys. Rev. A

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ABSTRACT

A recently synthesized and characterized homologous series of liquid crystal compounds (n4COOBC) is shown by high resolution a.c. microcalorimetry experiments (on the n=3,6 homologues) to most likely exhibit Smectic A to Smectic B (Hexatic) (SmB_H) phase transitions exclusively. This is in partial contrast to earlier tentative assignments, based on low resolution calorimetry, x-ray and microscopy studies, which had crystal smectic B (SmB_X) for n = 4-8 and SmB_H for n = 3 and 9. The observed SmA-SmB_H thermal anomalies exhibit strong fluctuation contributions but are clearly first order. Experimental results are compared with the extensively characterized n-alkyl-4' alkoxy-biphenyl-4-carboxylates (nmobe's) and discussed in the context of Goodby's empirical molecular structure rules for the existence of the SmB_H, and in the context of a generic phase diagram (SmA,B_X,B_H) recently predicted by Aharony et al. The latter illustrates the physical content of our earlier suggestion that short range hexagonal positional order is responsible for the ubiquitous tricriticality of the SmA-SmB_H phase transition.

I. Introduction

A new homologous series of liquid crystal compounds, the n-alkyl-4'-n-pentanoyloxy-biphenbyl-4-carboxylates (n4COOBC, n=1-12), recently synthesized and characterized by Surrendranath et al,[1] exhibited smecticA to Smectic B transitions for n = 3 - 9. The Smectic B phases for n = 3 and 9 were tentatively assigned as hexatic SmB phases[2] (SmB_H) based on microscope and low resolution X-ray studies; whereas for n = 4 - 8 the crystalB phase (SmB_X) was tentatively assigned.

High resolution a.c. microcalorimetry studies of the n = 3, 6 compounds reported here strongly suggest that n4COOBC compounds with $3 \le n \le 9$ exhibit SmA - SmB_H transitions exclusively.

The molecular structure (see Fig. 1) of the n4COOBC series is a small modification of the nmOBC series (n-alkyl-4'-alkoxy-biphenyl-4-carboxylates) synthesized and studied by Goodby[3] and rich in continuous SmA - SmB_H transitions. The modification, involving a change from alkoxy to acyloxy, is designed to weaken the lateral dipole moment of the molecule which, according to the empirical criteria of Goodby,[3] should shift the mesogenic behavior from hexatic toward the crystal phase. The results reported here indicate that the SmB_H phase persists in spite of the weakened lateral dipole. However the SmA - SmB_H transitions exhibit much stronger thermal anomalies, indeed they are clearly first order, than those found in the nmOBC series which are continuous (or nearly so). This is an interesting result because it is consistent with the generic phase diagram (Fig. 2) recently suggested by Aharony et al[4] which predicts that a change in the molecular interaction that moves materials exhibiting continuous SmA-SmB_H transitions toward SmA-SmB_X transitions, will merely yield first order SmA-SmB_H transitions, as observed here, if the change is too small. Thus on the generic diagram the nmOBC materials, which apparently show nearly tricritical behavior,[5] may lie near the tricritical point whereas the n4COOBC materials lie just to the right of it but still on the SmA-SmB_H portion of the line (see Fig. 2). If this scenario, which assumes Goodby's empirical rules and Aharony et al's qualitative theoretical analysis, is correct, it means that the range of lateral dipole moment strength spanned by these two homologous series is insufficient to produce materials which are 1) far enough to the left of the tricritical point (i.e., insufficiently strong lateral dipoles) to exhibit simple critical behavior or 2) far enough to the right (insufficiently weak lateral dipoles) to exhibit the SmB_X phase. Although the experimental evidence is not entirely convincing, and it is unlikely that lateral dipoles alone are at work, these results do suggest that continued synthetic efforts aimed at extending the physically accessible region of Fig. 2 are in order, and should be paralleled by high resolution microcalorimetry and X-ray experiments.

II. Experimental

The materials used in this study were purified by normal recrystallization procedures and by preparative high pressure liquid chromatography (HPLC). Area ratio analysis of analytical HPLC data indicated that the samples were ~99.9% pure. The specific heats were measured by an a.c. microcalorimetry technique described elsewhere[6] and used extensively in liquid crystal phase transition studies. The accuracy is probably not better than twenty percent. The heat capacity resolution, however, is approximately 0.5%, for sample size in the range 50-150 mg. The temperature resolution of the data reported here is 0.005K; being determined by the amplitude of the a.c. temperature oscillations.

III. Results and Discussion

Experimental results are shown in Figure 3 for 34COOBC and in Figure 4 for 64COOBC. These figures clearly show sharp breaks in the slope of the experimental specific heat data just above and below the peak (see arrows). We attribute these breaks to narrow two phase regions; which are likely due to a small residual impurity concentration or to strucural defects (perhaps induced by layer thinning on warming through the SmA-SmB_H transition[7]) coupled with the first order character of the transition. The existence of the two phase region casts serious doubts on the meaningfulness of the data between the arrows because the a.c. microcalorimetry technique is not adiabatic.

The data outside the arrows were fit to simple power laws of the form

$$C_p = At^{-\alpha} + B \qquad (1)$$

where $$t \equiv (T - T_c)/T_c \qquad (2)$$

and all parameters (A, α, T_c, B) were allowed to adjust. The results are given in Table I. The curves through the data in Fig. 3 are the best fits of the data and are quite good as the x^2 values and the figures themselves indicate. Because of the first order nature of the transition the constraints $T_c = T_c'$, $B = B'$, $\alpha = \alpha'$, taken collectively or in any combination, are unjustified and indeed destroy the quality of the fits. The first order character of the transition also makes the regions within ~ 0.2 - 0.5 K of the transition physically inaccessible (see Figs. 3 and 4 and $T_{min} - T_c$ and $T_c' - T_{max}$ in Table I) so the data span only a little more than a decade of reduced temperature. Therefore, the tabulated values of α and α' should be taken as only qualitatively correct i.e., one can say they are strongly positive. The high degree of similarity of the heat capacity anomoly in these two materials (n=3,6) and the strong fluctuation contributions make it very likely that these are SmA-SmB_H transitions and suggest that such a transition is common to this series for $3 \leq n \leq 9$.

It is interesting to note that the asymmetry of the transitions is the reverse of that at a normal, continuous λ-like transition. It is interesting, but not understood, that a much weaker asymmetry is present in 65OBC; where the anomaly is in fact very nearly symmetric.[7,8] The anomaly reverts to the usual asymmetry and is rapidly weakened as PP5CC (4-propionylphenyl-trans-(4-n-pentyl)-cyclohexane carboxylate) is added to 65OBC.[7] Thus it appears that the asymmetry is in the reverse sense in materials exhibiting strong SmA-SmB_H thermal anomalies and in the usual sense in those exhibiting weak thermal anomalies. Considering that 65OBC may be near a tricritical point[5,7] it is tempting to speculate that this reversal in the sense of the anomaly is related to the crossover from first order to critical with the tricritical point nearly symmetric. One must resist such a temptation because impurity renormalization almost certainly affects 65OBC/PP5CC thermal anomalies,[7] a technical problem which is under investigation.

The tricriticality vs. criticality problem[5,7] that has plagued the SmA-SmB_H transition since its discovery remains an important outstanding problem in liquid crystal physics. Our only direct contribution to that problem here is to note that the range of intermolecular interactions spanned by materials studied to date is apparently extremely narrow, as we pointed out in the discussion of Fig. 2.

In earlier work[7] we presented what we consider to be a quite compelling empirical evidence that coupling between short range hexagonal positional order (SRHPO) and bond orientational order (BOO) is a good candidate for tricriticality in the nmOBC series. That reasoning has been applied here, augmented by Goodby's criteria,[3] and aided by the illustrative use of Aharony et al's phase diagram, to explain the first order character of the n4COOBC SmA-SmB$_H$ transitions. The resulting picture is not only empirically consistent but is also consistent with our current theoretical understanding of the SmA-SmB$_H$ transition; e.g., as reflected in the model of Bruinsma and Nelson (BN).[8]

SRHPO and BOO are explicitly coupled in the BN free energy through an expression of the form

$$F_c = \tfrac{1}{2} \int_{\Lambda_0<q<\Lambda_1} d^2q\{A(\vec{q}) + B(\vec{q})|\Psi_0|\cos 6(\theta(\vec{q}) - \theta_0)\}|\rho(\vec{q})|^2 \qquad (3)$$

where

$$\Psi_0 = |\Psi_0|\, e^{i6\theta_0} \qquad (4)$$

is the complex (XY-like) BOO parameter and $\rho(\vec{q})$ is the Fourier component of intra-layer density at wavevector $\vec{q}$. $A(\vec{q})$ is the inverse density susceptibility at wavevector $\vec{q}$ and $B(\vec{q})$ measures the $\vec{q}$ dependent coupling between SRHPO and BOO. This form is valid when the range of SRHPO is small compared with that of BOO. It ignores interlayer coupling. The domain of integration in Eqn. 4 spans the diffuse peak of the in plane x-ray structure factor ~ $<|\rho(q)|^2>$. In the absence of a term in the free energy coupling positional and bond orientational order there would be no diffuse 6-fold symmetric X-ray signature for the SmB$_H$ phase, contrary to experimental evidence.[2,9]

Therefore, the X-ray signature of the SmB$_H$ phase in all systems studied to date and the strong increase in the in plane positional correlation length at the SmA-SmB$_H$ transition[2,9] that Eqn. 3 or a comparable form is necessary to explain known SmB$_H$ phenomenology. It is straightforward to integrate out the short range density fluctuations, $\rho(\vec{q})$. This leads to a renormalization of the coefficients of the SmB$_H$ Landau model[8]

$$F = r\,|\Psi_0|^2 + u\,|\Psi_0|^4 + \ldots \tag{5}$$

where

$$r = r_0\,(T-T^*) \text{ and } u > 0. \tag{6}$$

The corrections are of the form

$$F_c = F_0 + \sum_n \alpha_n\,|\Psi_0|^{2n}. \tag{7}$$

F_0 is a term independent of Ψ_0 and

$$\alpha_n = \frac{-1}{2\pi} \int_{\Lambda_0}^{\Lambda} qdq \left[\frac{(2n-1)!!\,b^{2n}(\vec{q})}{2^{n+1}nn!} \right] < 0 \tag{8}$$

where

$$b(\vec{q}) = B(\vec{q})/A(\vec{q}). \tag{9}$$

Note that corrections are negative at all orders in $|\Psi_0|^2$; resulting in an elevated transition temperature ($T_c = T^* - \alpha_1/r_0$) and a reduced fourth power coefficient ($u + \alpha_2$), where

$$\alpha_1 = -\frac{1}{8\pi} \int_{\Lambda_0}^{\Lambda_1} b^2(\vec{q})\; qdq, \tag{10}$$

and

$$\alpha_2 = \frac{-3}{64\pi} \int_{\Lambda_0}^{\Lambda_1} b^4(\vec{q})\; qdq. \tag{11}$$

The negative contribution, α_2, that F_c makes to the fourth power coefficient (Eqn. 11) can, of course, drive an otherwise continuous transition discontinuous or, at least, toward tricriticality. It is important to be reminded that $A(\vec{q})$, the denominator of $b(\vec{q})$ (Eqns. 8,9), which determines the magnitude of the correction to α_2 (Eqn. 11), will be smallest for $q \sim q_0$, ($q = q_0$ maximizes $\langle|\rho_q|^2\rangle$) and that $A(q_0)$ must vanish at the hypothetical, continuous SmB_H-SmB_X transition (by Landau theory symmetry arguments this transition must normally be discontinuous) where $\langle|\rho(\vec{q}_0)|^2\rangle$ diverges. This means that $b(q_0)$ can be large if the SmA-SmB_H transition is close, in the thermodynamic sense, to the SmB_H-SmB_X transition; leaading to enhanced (negative) values of α_2 and the tendency twoard tricriticality and/or first order behavior. The ubiquity of SmB_X phases and the paucity of SmB_H phases suggests that the SmB_X (or SmE) phase is always lurking near-by in systems with SmA-SmB_H phase transitions, as does the X-ray evidence.[2,9] This and other[7] empirical evidence supports the BN model of the SmB_H phase, Aharony's phase diagram and our previous discussion of SmA-SmB_H phase phenomenology.

IV. Conclusions

High resolution a.c. microcalorimetry experiments on the n4COOBC series have demonstrated rather clearly that first order SmA-SmB_H phase transitions exist. The relative strength of the thermal anomalies in the n4COOBC and nmOBC homologous series; i.e., the fact that the anomaly is first order in the materials with the weaker lateral dipole moment (n4COOBC) and continuous, or nearly so, in the others (nmOBC), supports our contention that SRHPO drives the SmA-SmB_H transition toward tricriticality or beyond as illustrated by the generic phase diagram of Aharony et al[4]; given that Goodby's empirical rules[3] apply to these materials. By implication the materials studied thus far probe only a very narrow range of intermolecular interactions.

The internal consistency of these ideas supports our previous suggestion[7] that SmA-SmB_H tricriticality (in contrast to the SmB_H phase) is ubiquitous in liquid crystals due to the pervasiveness of positional order fluctuations (SRHPO); which may in fact be prerequisite to the formation of the SmB_H phase in materials studied to date. The SmB_H may, therefore, be is a fluctuation induced phase; arising for much the same reason as the biaxial nematic in the Grinstein and Toner model of the nematic-SmecticA-SmecticC multicritical point,[10] though without the complications of defect mediated melting. The Bruinsma Nelson model[8] of the SmB_H is consistent with the picture we have given and, indeed, suggests it. We stress that we are not suggesting that all SmB_H phases need be fluctuation induced, but only that known phenomenology strongly suggests it for materials studied thus far. The dearth of SmB_H phases generally (by comparison with SmB_X (or E) phase) suggests that the need for SRHPO may extend well beyond the two classes of compounds discussed here; apparently the SmB_X (or E) wins the competition most often because their fluctuations, and hence closely proximate phases, are prerequisite to SmB_H formation.

Although the above scenario is appealing it should only be used as a working hypothesis because there still exists somewhat puzzling empirical evidence; namely the extensive heat capacity studies of Pitchford et al[5] on the nmOBC series which yielded large positive values of α in materials where the crystal phase, SmE in this case, is probably several tens of degrees below the $SmA-SmB_H$ transition. X-ray experiments on those materials would tell us whether SRHPO is still playing an important role. Similar measurements should be performed on the 65OBC/PP5CC mixtures studied previously in this laboratory;[7] which showed some evidence of being far removed from the effect of parasitic fluctuations. Mixture systems, however, are subject to the complication of Fisher renormalization of critical exponents. The ideal approach is to make further modifications of the nmOBC molecular structure designed to expand the range of molecular interactions probed (see Fig. 2). At question is the existence of ideal

SmA-SmB_H criticality in one extreme (small x, where x = lateral dipole moment in Goodby's scheme) and SmA-SmB_X transitions in the other (large x). One of us (VS) is currently engaged in the synthesis of such materials.

We gratefully acknowledge the support of the NSF Solid State Chemistry Program under grants DMR87-03524 and DMR 85-15221. ✓

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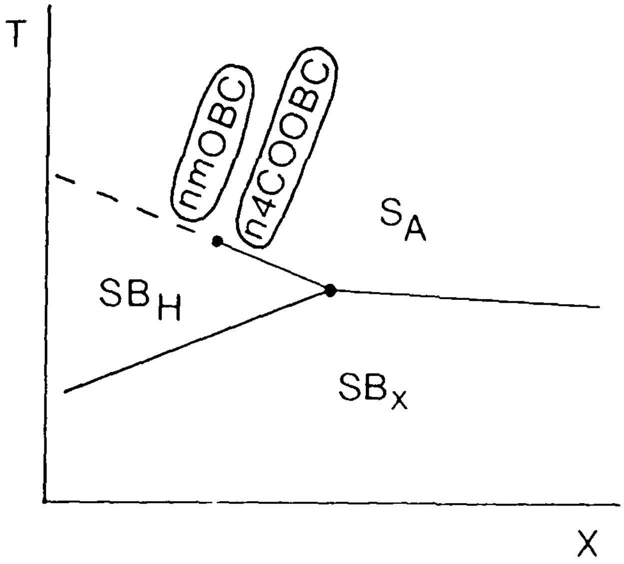
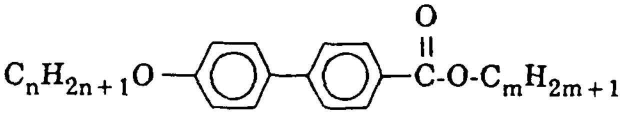
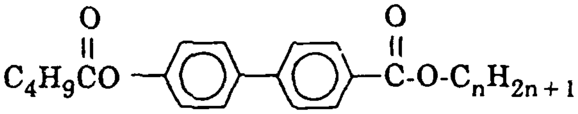
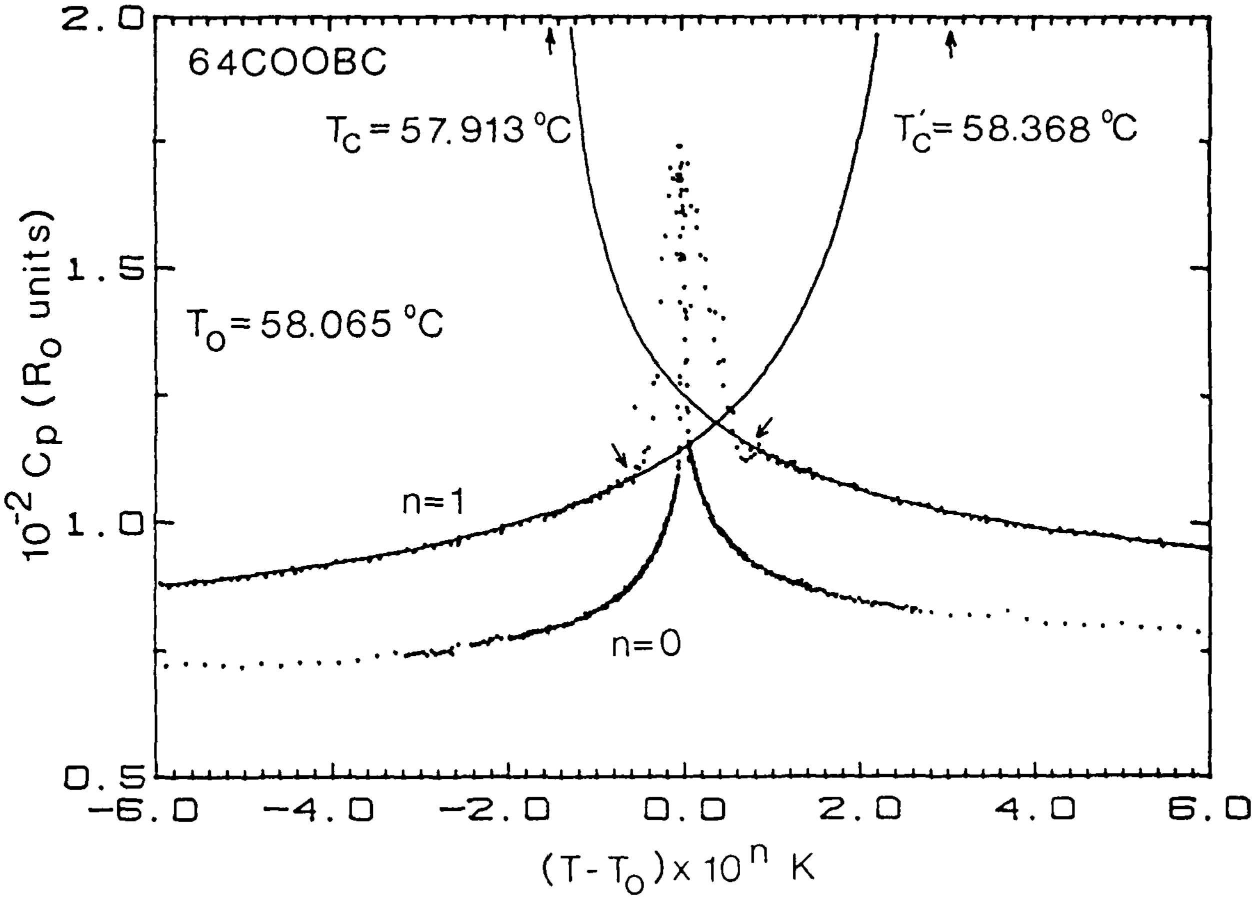

T
nmOBC
n4COOBC
S_A
SB_H
SB_X
X

nmOBC

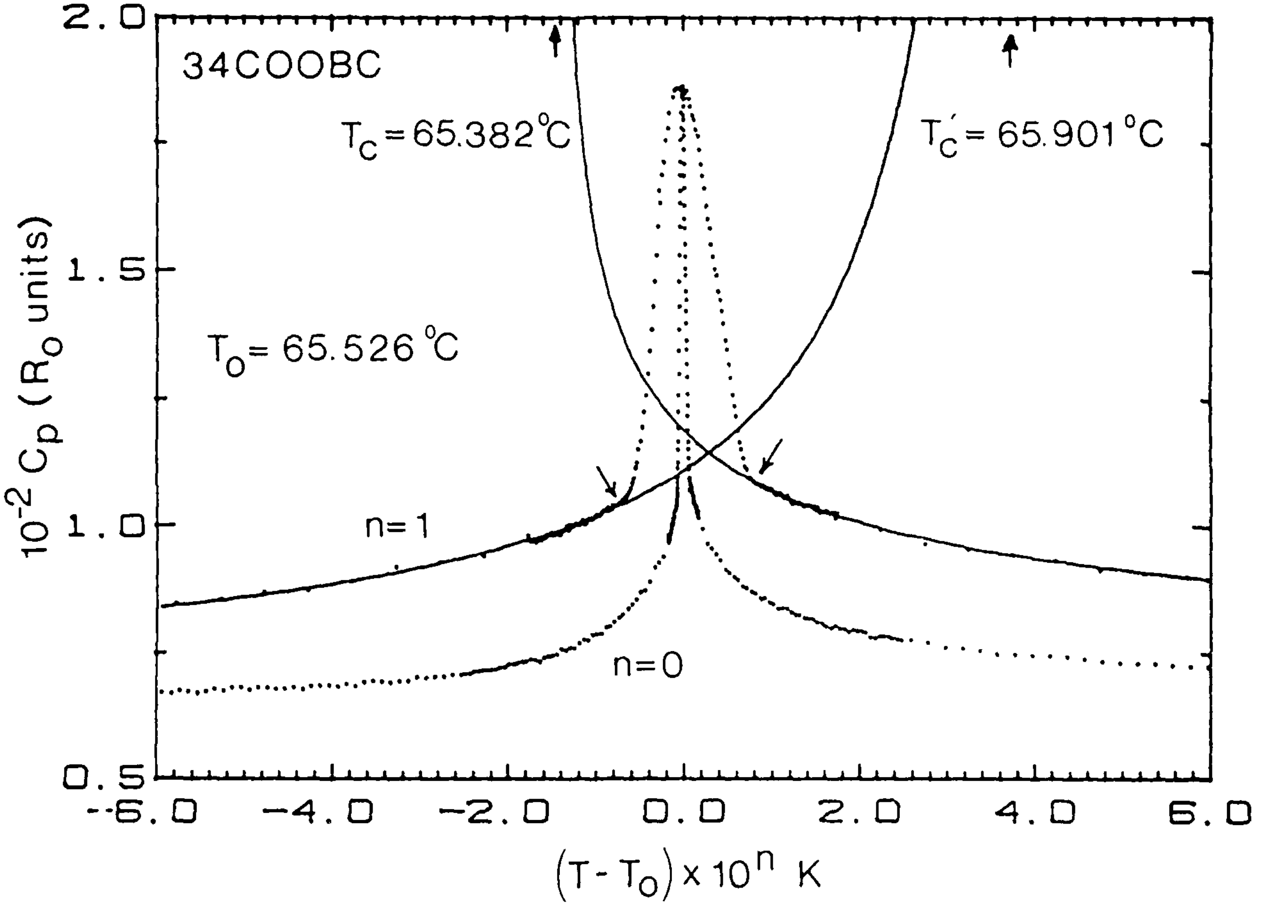


n4COOBC





64COOBC
$T_c = 57.913$ °C
$T_c' = 58.368$ °C
$T_o = 58.065$ °C
n=1
n=0
2.0
1.5
1.0
0.5
$10^{-2} C_p$ (R_o units)
-6.0
-4.0
-2.0
0.0
2.0
4.0
6.0
$(T - T_o) \times 10^n$ K


34COOBC
$T_c = 65.382^\circ C$
$T_c' = 65.901^\circ C$
$T_o = 65.526^\circ C$
n=1
n=0
$10^{-2} C_p$ (R_o units)
$(T - T_o) \times 10^n$ K
2.0
1.5
1.0
0.5
-6.0
-4.0
-2.0
0.0
2.0
4.0
6.0

	A (A')	B (B')	α (α')	T_c (°C) (T_c')	T_c-T_{min} K (T_{max}-T_c')	χ^2 ($\chi^{2'}$)
34COOBC	2.313	60.032	0.4167 ± 0.02	65.3825	0.219	0.82
	(0.132)	(62.735)	(0.8667 ± 0.04)	(65.9015)	(0.450)	(1.23)
64COOBC	1.432	69.277	0.4764 ± 0.02	59.9126	0.238	1.67
	(0.227)	67.196	(0.7627 ± 0.03)	(58.3677)	(0.367)	(1.61)

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