

Calorimetric evidence for the existence of an intermediate phase between the ferroelectric nematic phase and the nematic phase in the liquid crystal RM734

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(Received 21 February 2024; accepted 27 June 2024; published 17 July 2024)

The idea that rodlike molecules possessing an electric dipole moment could exhibit a ferroelectric nematic phase was suggested more than a century ago. However, only recently such a phase has been reported for two quite different liquid crystals: RM734 [4-[(4-nitrophenoxy)carbonyl]phenyl 2,4-dimethoxybenzoate] and DIO [2,3',4',5'-tetrafluoro[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate]. For RM734 a direct ferroelectric nematic (N_F) to classical nematic N transition was reported, whereas for DIO an intermediate phase N_x was discovered between the N_F and the N phases. Here we present high-resolution calorimetric evidence that an intermediate N_x phase also exists in RM734 along a narrow temperature range between the N_F and the N phases.

DOI: [10.1103/PhysRevE.110.014703](https://doi.org/10.1103/PhysRevE.110.014703)

I. INTRODUCTION

Liquid crystals (LCs) exhibit a large number of phases with different degrees of orientational and partial positional order between the liquid and the crystalline solid state [1,2]. For rodlike, thermotropic liquid crystals, the least ordered phase is the nematic phase, in which the molecules exhibit long-range orientational order but no long-range positional order. However, several modifications of nematic order have been observed. Chiral LC molecules form a twisted nematic (so-called cholesteric) phase and, for higher chirality, they may also exhibit blue phases forming lattices of defect lines. Transitions between two uniaxial nematic phases with short-range smectic order have been observed [3]. Also, nematic-nematic phase transitions were discovered for nonchiral dimer molecules [4,5].

More than a century ago Debye [6] and Born [7] argued that the presence of molecular dipoles could result in long-range ferroelectric nematic type of order. Such a phase has never been observed until recently. In two independent reports, published in 2017, Mandle *et al.* [8] and Nishikawa *et al.* [9] reported the discovery of a new type of nematic phase for two different molecules. These two compounds are referred to as RM734 [4-[(4-nitrophenoxy)carbonyl]phenyl 2,4-dimethoxybenzoate] [8] and DIO [2,3',4',5'-tetrafluoro[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxan-2-yl) benzoate] [9]. The strongly polar compound RM734 was reported to exhibit two nematic phases that are separated by a first-order transition [10]. Chen *et al.* [11] presented evidence for ferroelectricity for the low-temperature nematic phase (N_F) of RM734, and normal nematic uniaxiality for the high-temperature one. DIO exhibits in addition to the low-temperature N_F phase, an intermediate phase situated between

the N_F and the classical nematic phase N [9]. The true nature and the name for the intermediate phase is still a matter of extensive debate. This phase was initially called M_2 [9], and subsequently N_x [12], SmZ_A [13], and N_S [14], considering either a smectic type of order with the molecular axis perpendicular to the layer normal or a splay nematic phase, respectively. Because calorimetry cannot render information on the structure of phases, and in view of the above variations in the nomenclature of the intermediate phase, and being consistent with our previous paper [15], we henceforth use N_x to indicate the phase between the N and the N_F phases.

In high-resolution adiabatic scanning calorimetry (ASC) measurements (carried out in 2020) of the N - N_F transition of RM734, the order of the transition as well as the pretransitional fluctuation-induced critical behavior was investigated in detail [16]. The N - N_F transition was found to be very weakly first order with a latent heat $L = 0.115 \pm 0.005$ J/g. Power-law analysis of the specific heat capacity in both phases resulted in an effective critical exponent $\alpha = 0.50 \pm 0.05$. This value and the small latent heat suggest the N - N_F phase transition in RM734 to be close to a tricritical point. In a paper submitted in 2021 and published in 2022, Chen *et al.* [17] studied binary mixtures of DIO and RM734 by means of optical microscopy, differential scanning calorimetry, polarization measurements, and small-angle x-ray scattering experiments and showed complete miscibility of the isotropic phase, and the N and N_F phases. The N_x phase present in DIO persisted only in mixtures with concentrations above 40% of DIO, indicating a possible triple point around that concentration. In the second half of 2021 and the first half of 2022 some of us carried out detailed high-resolution adiabatic scanning calorimetry measurements on DIO and of binary mixtures with RM734 for concentrations above 10% weight fraction

of DIO. Contrary to the results reported in Ref. [17], we found that the intermediate N_x phase was present for all studied mixtures, albeit with a strongly decreasing temperature range with decreasing concentration of DIO. Both the N - N_x and the N_x - N_F transitions were found to be first-order ones, with very small latent heats [15]. Since high-resolution data existed [16] for RM734, we did not remeasure it at that time. However, Sebastián *et al.* [14] conjectured the possibility of the existence of a very narrow N_x phase also in RM734. Their conjecture was based on the observation of freezing of the nematic fluctuations in a very small temperature range in the N phase close to N_S , similar to what was observed for N_x in DIO. Although, in our previous work on RM734 we did not observe any thermal signature of a possible N - N_x transition [16], we have made further efforts to improve the resolution of the measurements and revisit the RM734 problem. In this paper, we present new ASC results obtained for 20 scanning (heating and cooling) runs on five RM734 samples from four different batches.

II. EXPERIMENT

A. Adiabatic scanning calorimetry

ASC yields simultaneously and continuously the temperature evolution of the heat capacity C_p and the enthalpy H of a sample [18–21]. Contrary to all other calorimetric methods operating with a constant scanning rate, in ASC a constant heating or cooling power is applied to a sample holder containing the sample. This holder with a sample is placed inside a surrounding adiabatic shield. The adiabatic conditions are maintained by means of a number of shields surrounding the sample holder and sample, as well as by pumping the air from the calorimeter.

Detailed descriptions of the “classical” ASC implementations and results can be found in [18–21], and references therein. A problem in the older types of ASCs lies in maintaining adiabatic conditions over long time and wide temperature ranges. In the past decade the development of the novel Peltier-element-based adiabatic scanning calorimeter (pASC) has largely eliminated these issues, with greater user-friendliness and much wider temperature ranges as well as much smaller samples (typically a few tens of milligrams) [22–24].

In a pASC heating run, the heat exchange between the inner shield and the sample holder is canceled by keeping the temperature difference, measured by a Peltier element, zero at all times, using a proportional-integrating (PI) control loop. In a cooling run, the PI control keeps a nonzero voltage offset, allowing one to control and monitor the heat exchange. During any run, the sample temperature $T(t)$ is recorded as a function of time t . Together with the applied power P this directly results in the enthalpy curve

$$H(T) - H(T_0) = \int_{t_0}^{t(T)} P dt = P[t(T) - t_0(T_0)], \quad (1)$$

where $H(T_0)$ is the enthalpy of the system at temperature T_0 at the starting time t_0 of the run. The heat capacity $C_p(T)$ is then calculated from the ratio of the known constant power P and

the changing temperature rate $\dot{T} = dT/dt$,

$$C_p = \frac{P}{\dot{T}}. \quad (2)$$

The specific heat capacity $C_p(T)$ and the specific enthalpy $h(T)$ are obtained by using the sample mass and the calibrated background values of the empty calorimeter and of the used sample cells. Keeping P constant in Eq. (2) is completely opposite to the operation of a differential scanning calorimeter, where a constant rate $\dot{T}$ is imposed on a sample and on a reference and where the difference in heat flux, $\Delta P(t)$, between the sample and the reference, is measured.

B. Materials and samples

The samples 1-UCO and 2-UCO named in Table I were both from the same batch of RM734 synthesized at the Soft Materials Research Center of the University of Colorado, USA (UCO). The samples 1-HULL-2, 1-HULL-3, 2-HULL-3, and 3-HULL-3 were from two different batches of RM734 (HULL-2 and HULL-3), synthesized at the Organic and Materials Chemistry Group of the Chemistry Department of the University of Hull, UK (HULL). RM734 material from batch HULL-1 has been used in preparing mixtures with DIO [14]. The samples 1-INSTECH and 2-INSTECH were from RM734 material purchased from INSTECH Inc., Boulder, CO, USA (INSTECH Inc). All compounds were used as received at the Laboratory for Soft Matter and Biophysics, Department of Physics and Astronomy, KU Leuven, Belgium. The samples (typically from 30 to 60 mg) were transferred into stainless-steel sample holders (Mettler Toledo 120 μ l medium pressure crucible) and hermetically sealed. These crucibles are vacuum-tight-closed with a miniature elastic O-ring between the cell body and the lid.

III. RESULTS AND DISCUSSION

A. Specific heat capacity

Similar to classical ASC, pASC measurements also yield simultaneously the temperature dependence of the specific enthalpy $h(T)$ and of the specific heat capacity $c_p(T)$. However, in looking at small features for a possible N - N_x transition temperature, it turned out that possible small variations in $h(T)$ near the expected transition were largely obscured by the large nonlinear temperature-dependent pretransitional background related to the transition to the N_F phase. Therefore, in the present study, we have focused on $c_p(T)$, which is the temperature derivative of $h(T)$, and more sensitive to effects that occur over a narrow temperature range.

In Table I, an overview of the different (heating and cooling) runs that are presented further on is given. Apart from run 1 (measured in August 2020), published in Ref. [16], all other runs in the table correspond to more recent efforts to look for convincing evidence of an N - N_x transition with settings of the calorimeter that were aimed at improved resolution and stability. In Table I, the first column is the run number and the second column is the date of the measurement. The third column gives the identifying name of the sample measured in a given run. In the name of the sample, the digit in front gives the sample number of a given batch. The acronyms stand

TABLE I. Identification and results for all the runs carried out in search of the existence of a N_x - N transition in RM734. From left to right, the number and date of the run, the origin and the mass of the sample, the type of run (heating or cooling), the average scanning rate, the transition temperatures $T_{N_F-N_x}$ and T_{N_x-N} , as well as the range ΔT of the N_x phase are presented.

Run No.	Date	Sample	Mass (mg)	Run type	Average rate (K min ⁻¹)	$T_{N_F-N_x}$ (°C)	T_{N_x-N} (°C)	ΔT (K)
1	2020.08.02	1-UCO	60.1	Heating	0.0301	131.65		
2	2022.11.04	2-UCO	33.4	Cooling	-0.0375	131.09	132.33	1.24
3	2022.11.03	2-UCO	33.4	Cooling	-0.0259	131.03	132.20	1.17
4	2022.10.31	2-UCO	33.4	Cooling	-0.0209	130.94	132.08	1.14
5	2022.11.01	2-UCO	33.4	Heating	0.0095	130.93	132.06	1.19
6	2022.11.03	2-UCO	33.4	Heating	0.0192	131.05		
7	2022.10.29	2-UCO	33.4	Heating	0.0385	131.14	132.32	1.18
8	2022.10.31	2-UCO	33.4	Cooling	-0.0161	131.06	132.29	1.23
9	2022.11.07	1-UCO	60.6	Cooling	-0.0187	130.88	132.06	1.18
10	2022.11.10	1-UCO	60.6	Cooling	-0.0235	131.13	132.33	1.2
11	2022.11.08	1-UCO	60.6	Heating	0.0083	131.10	132.31	1.21
12	2023.03.20	1-UCO	60.6	Heating	0.0345	130.89	132.11	1.22
13	2023.03.21	1-UCO	60.6	Cooling	-0.0656	130.86	132.08	1.22
14	2022.12.25	1-HULL-2	29.3	Free cooling	-0.0909	127.37	128.39	1.02
15	2022.03.28	1-HULL-3	28.9	Cooling	-0.0707	128.34	129.38	1.04
16	2023.03.28	2-HULL-3	28.9	Heating	0.0399	128.43	129.51	1.08
17	2023.03.29	3-HULL-3	28.9	Heating	0.0199	128.34	129.37	1.03
18	2023.11.28	1-INSTEC	27.8	Cooling	-0.0287	126.79	127.91	1.12
19	2023.12.22	2-INSTEC	65.9	Cooling	-0.0238	126.26	127.34	1.08
20	2023.12.26	2-INSTEC	65.9	Cooling	-0.0246	126.34	127.53	1.19

for the origin of the material (see Sec. II B). The digit after the acronym gives the number of the batch where appropriate. Further columns in the table give additional information regarding the sample mass, the type of the run (heating or cooling), an average value for the scanning rate, the observed values for the N_F - N_x and N_x - N transition temperatures, and the temperature width of the N_x phase. Regarding the rates, it should be noted that these are only average values, because in ASC runs the applied (heating or cooling) power is kept constant and the temperature-dependent rate (slowing down at phase transitions) is measured [see Eq. (2)].

In Fig. 1, the original data from Ref. [16] are compared with the results of a cooling run of a second sample of the same batch of RM734. As indicated by the arrow, there is a small peak visible about 1 °C above the N_F - N_x transition temperature. The existence of this feature is confirmed in Fig. 2 for a cooling run (run 10) as well as for a heating run (run 12) for the same sample in the same sample cell as measured in Ref. [16]. Thus, the indication for the existence of an intermediate N_x phase between the N_F and the N phases is present in two different samples of the same (UCO) RM734 batch. Figures with data from different runs on the same samples can be found in the Supplemental Material [25]. Figure 3 depicts the results of a cooling and a heating run for two different samples from batch HULL-3. In both cases a very small peak points at the presence of a N_x - N transition again about 1 °C above the N_F - N_x transition. This is confirmed in Fig. 4 by a cooling run for another sample from the same batch and a cooling run for a sample from the HULL-2 batch. The run for the latter sample was special in the sense that it was not obtained upon cooling with the cooling power kept constant, but in free cooling with the sample initially at 145 °C and the first (adiabatic) shield kept at a constant temperature of 100 °C. More recently we purchased RM734 from the commercial supplier INSTEC Inc

(USA) and performed additional pASC measurements. The $c_p(T)$ results for both runs are given in Fig. 5. Here evidence for a weak N_x - N transition is also present. In the Supplemental Material $c_p(T)$ figures for the other runs not discussed here can be found.

B. Transition temperatures and width of the N_x phase

In columns 7 and 8 of Table I the transition temperatures [maxima of the $c_p(T)$ peaks] of the N_F - N_x and N_x - N transitions are given. As can be seen in Fig. 6, quite substantial differences are observed between the different batches of the RM734 material. The transition temperatures fall in the temperature range between 126 °C and 132 °C. In the ninth column of Table I also the widths, ΔT , of the N_x phase observed for the different runs are listed. Here, and in Fig. 6, no clear batch dependence can be observed. The ΔT values vary between 1.02 and 1.24 K. This results in an average value of $\Delta T = 1.15 \pm 0.10$ K for the width of the N_x phase of RM734. In the phase diagram shown in Fig. 8 of Ref. [15] for mixtures of DIO and RM734, in addition to the reported data points for the transition temperatures, also quadratic trendlines through the N_F - N_x data points and the N_F - N_x ones, are displayed. Extrapolation of these two trend lines to zero DIO concentration results in a width for N_x in RM734 of $\Delta T = 0.89$ K, which is close to the above average value.

It is remarkable that the transition temperatures for the onset of the N_F phase in RM734, which are reported here and have been reported by a number of groups [8,14,17], vary according to publications by up to ~ 7 K (in the range from 126 °C to 133 °C). This is indeed a large variation, too high to be solely attributed to small amounts of organic impurities, for which usually changes of 1–2 K are found. Standard characterization techniques used by most authors do

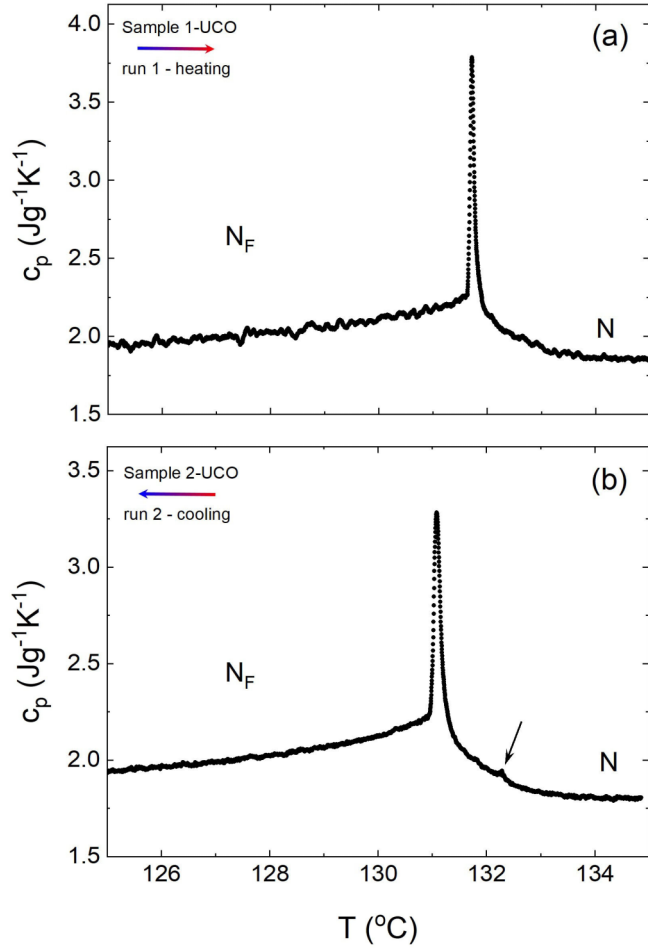


FIG. 1. Temperature dependence of the specific heat capacity $c_p(T)$ of the ferroelectric nematic liquid crystal compound RM734. (a) Data from the heating run 1 for sample 1-UCO from Table I and Ref. [16]. (b) Data from cooling run 2 for sample 2-UCO from Table I. The arrow indicates the location of the N_x - N transition.

not record very small amounts of inorganic ions. As the terminus of the RM734 molecule contains a “nitro” group, which in chemistry is used to form complexes with cations to form crystals, we surmise that during the purification processes very small ions (e.g., Na^+ , K^+ , Mg^{2+}) of various elements and in different amounts might be present and are coordinating dynamically with the nitro group. It is well known from the area of organometallic LCs that the complexation of organic groups can modify (i.e., decrease or increase) phase transition temperatures.

C. Transition heat of the N_x - N transition

In the figures discussed so far, and for the temperature ranges where the two transitions N_F - N_x and N_x - N are present, the $c_p(T)$ peak for N_x - N is extremely small in comparison with the one for N_F - N_x . The visibility of the N_x - N peak can be substantially improved by reducing the $c_p(T)$ and T range around the transition. This is done in the top part of Fig. 7 for the heating run 12, where the peak is clearly visible on top of the substantial pretransitional background increase (with decreasing temperature) associated with the N_F - N_x transition. From

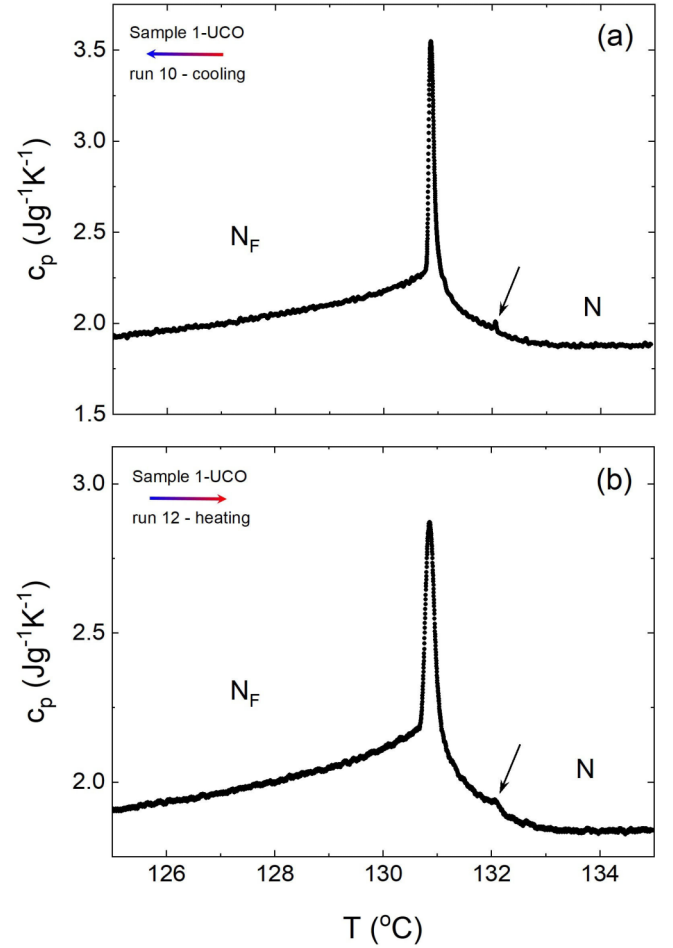


FIG. 2. Temperature dependence of the specific heat capacity $c_p(T)$ of the ferroelectric nematic liquid crystal compound RM734. (a) Data from the cooling run 10 for sample 1-UCO from Table I. (b) Data from heating run 12 for sample 1-UCO from Table I. The arrow indicates the location of the N_x - N transition.

this figure it is also possible to derive the transition heat Δh of the N_x - N transition by integrating the part of the experimental curve above the background given by the solid curve. This curve is a fit to the $c_p(T)$ data between 131.5 °C and 132.5 °C, excluding the range corresponding with the N_x - N transition. The corresponding integration result is displayed in the lower part of Fig. 7. From careful inspection of this curve, it can be concluded that the specific enthalpy change Δh needed to convert from the N_x to the N phase is $\Delta h = 0.0045 \pm 0.0005$ J/g. Similar analyses for other runs gave similar values for Δh . It should be noted that Δh includes the true latent heat L and the pretransition enthalpy increase δh . Based on comparison with DIO the value of Δh is most likely equal to the latent heat. This value is extremely small in comparison with $L = 0.115 \pm 0.005$ J/g for the N_F - N_x transition and 2 J/g typical for a normal isotropic-nematic transition. In Fig. 10 of Ref. [15] for mixtures of DIO and RM734, in addition to the reported data points for the latent heats, also quadratic trendlines through the N_F - N_x data points and the N_x - N ones are displayed. Extrapolation of the trend line of N_x - N to zero DIO concentration results in a value of $L = 0.0042$ J/g, which

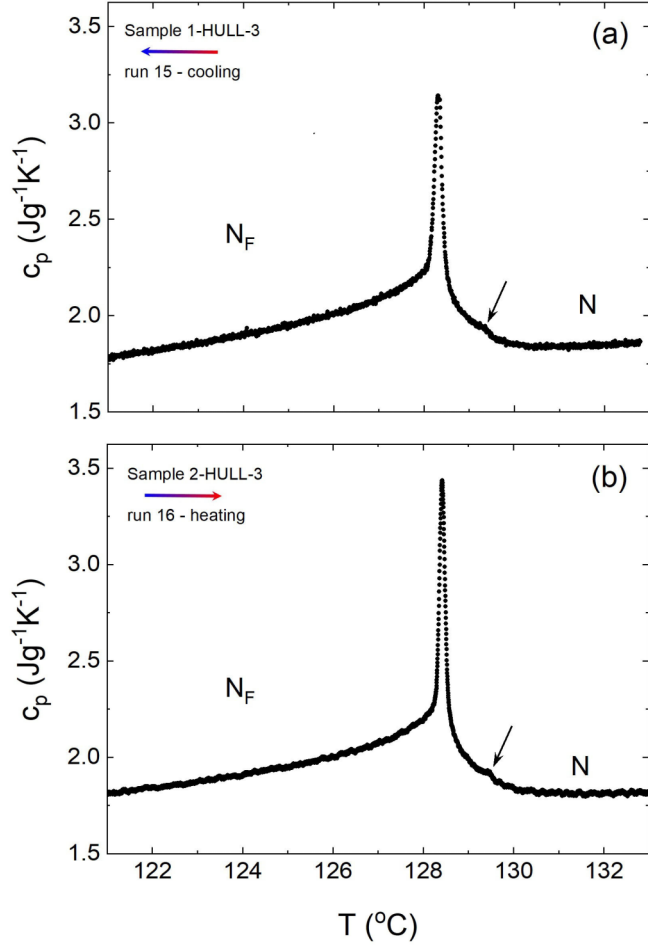


FIG. 3. Temperature dependence of the specific heat capacity $c_p(T)$ of the ferroelectric nematic liquid crystal compound RM734. (a) Data from the cooling run 15 for sample 1-HULL-3 from Table I. (b) Data from heating run 16 for sample 2-HULL-3 from Table I. The arrow indicates the location of the N_x - N transition.

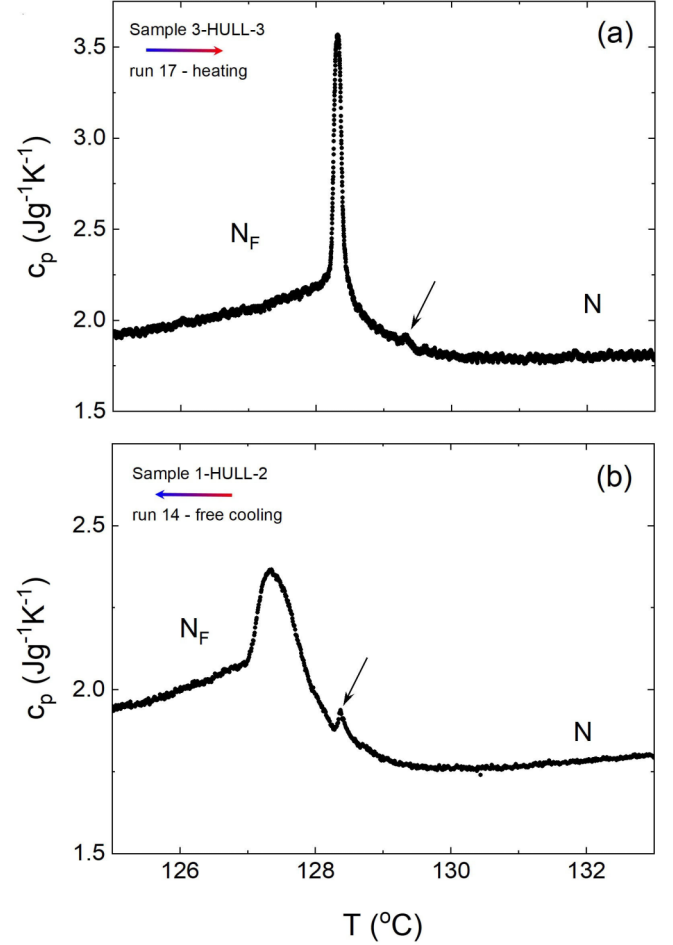


FIG. 4. Temperature dependence of the specific heat capacity $c_p(T)$ of the ferroelectric nematic liquid crystal compound RM734. (a) Data from the heating run 17 for sample 3-HULL-3 from Table I. (b) Data from free cooling run 14 for sample 1-HULL-2 from Table I. The arrow indicates the location of the N_x - N transition.

is quite close to the value $L = 0.0045 \pm 0.0005$ J/g derived from Fig. 7.

D. On the nature of the N_x phase of RM734

Presently, there is no direct structural information available on the nature of the N_x phase of RM734 which is clearly visible in a narrow temperature range in the presented pASC results. Such tests (optical or by x rays) are not straightforward due to the quite narrow temperature range and would require temperature scanning rates and stability approaching those as in pASC presented here. Although from calorimetric results no structural information can be derived, the combination of the current results with other recent thermodynamic and structural studies in related systems, in particular mixtures of RM734 with other compounds, presents convincing evidence for the N_x phase of RM734 being the same as the N_x phase of DIO (or SmZ_A as this phase is called by the Boulder group [13,17]).

Experiments performed by the Boulder group [17] have shown that as long as the SmZ_A can be distinguished in mixtures of RM734 and DIO as a separate phase (down to

concentrations of about 40%), it behaves similar as pure DIO. In a recent calorimetric study of mixtures of RM734+DIO by the Leuven group [15] of the concentration range down to 10% of DIO a N_x (SmZ_A) phase with a temperature range of about 1 K or more was detected. As pointed out in Sec. III B, extrapolation of the N_F - N_x and the N_x - N transition lines to 0% DIO (i.e., pure RM734), projected a width of 0.89 K for the N_x phase of RM734, consistent with the pASC measured ranges reported here. This indicates the continuity of the N_x phase over the full concentration range from pure RM734 to pure DIO, and the same phase for both pure components. This is fully consistent with the empirical rule formulated by Sackmann and Demus [26,27] stating that all crystalline modifications which exhibit complete miscibility in binary systems, can be marked with the same symbol.

In recent reports on mixtures of RM734 and ionic liquids (IL; at low concentrations) [28] and DIO and an ionic liquid [29], clear evidence was obtained for a SmZ_A in cases of DIO+IL and RM734+IL up to very low concentrations of IL. Thus, a SmZ_A phase (initially named M_A in [28]) is indicated also in pure RM734.

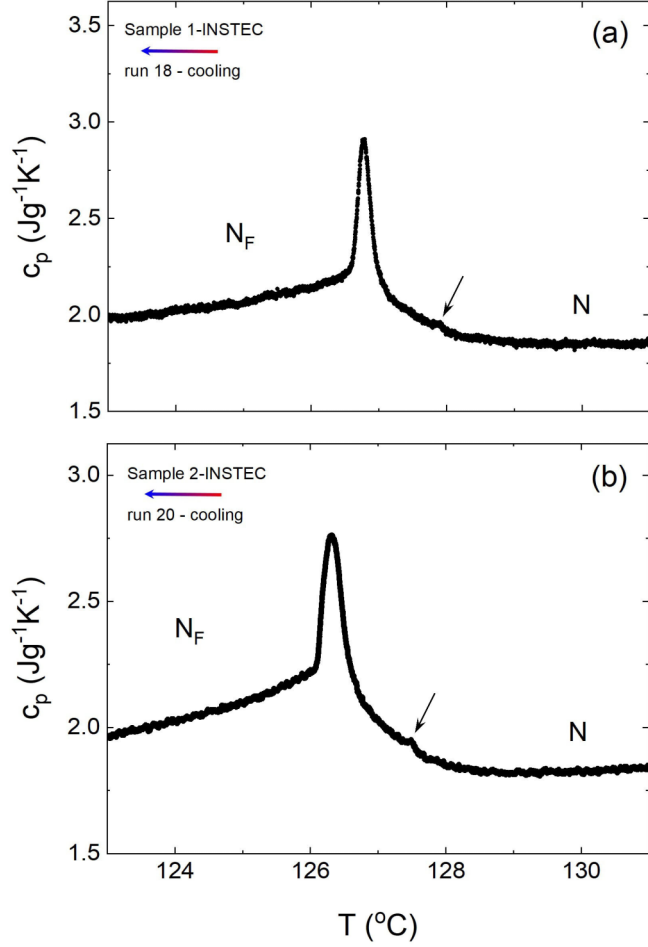


FIG. 5. Temperature dependence of the specific heat capacity $c_p(T)$ of the ferroelectric nematic liquid crystal compound RM734. (a) Data from the cooling run 18 for sample 1-INSTEC from Table I. (b) Data from cooling run 20 for sample 2-INSTEC from Table I. The arrow indicates the location of the N_x - N transition.

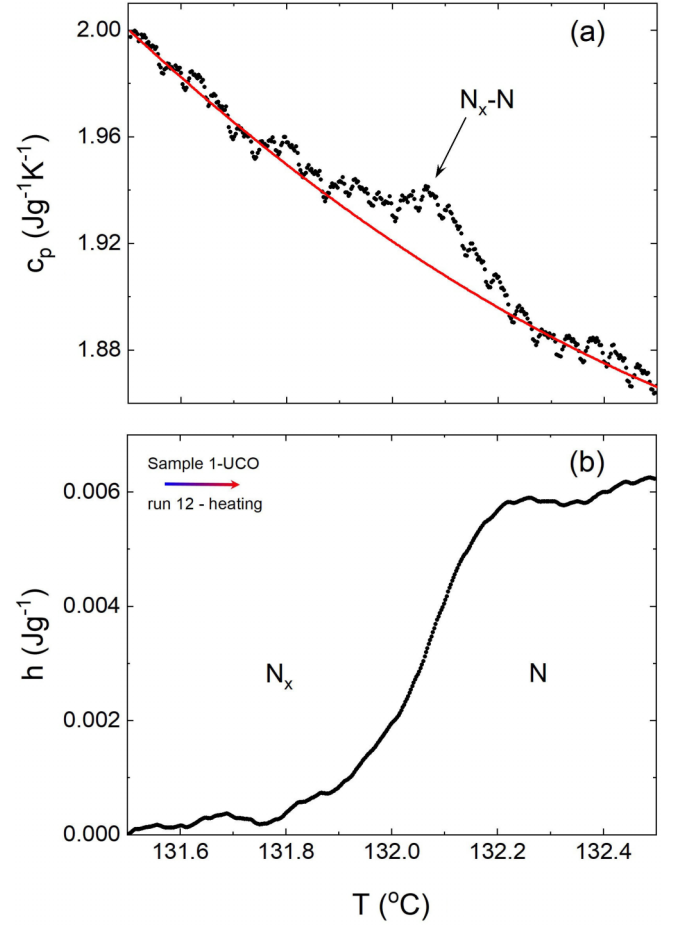


FIG. 7. (a) Temperature dependence of the specific heat capacity $c_p(T)$ of the ferroelectric nematic liquid crystal compound RM734 in a narrow temperature range around the N_x - N phase transition temperature. (b) Enthalpy increase, associated with transition, derived from the integration of the difference between the experimental $c_p(T)$ data and the solid background curve in (a).

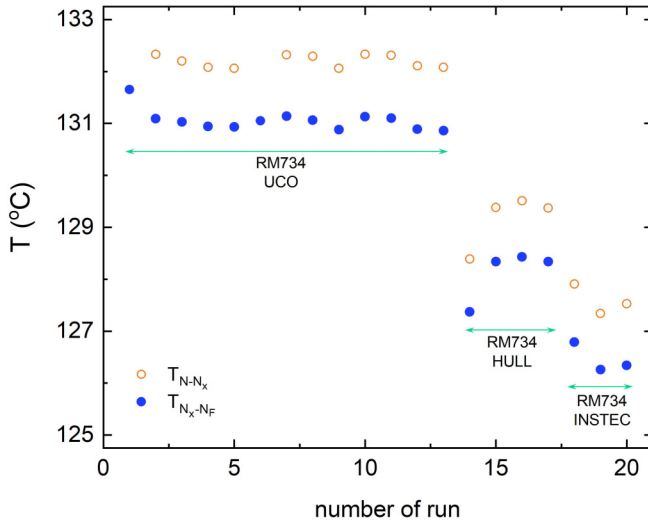


FIG. 6. Transition temperatures of the N_F - N_x (open circles) and N_x - N (closed circles) transitions of RM734 as obtained from the pASC measurements of the different runs of Table I.

In a paper by Chen *et al.* [13], the SmZ_A phase was characterized as antiferroelectric, with the nematic director and the polarization P oriented parallel to smectic layer planes, and the polarization alternating in sign from layer to layer with a 180° period. A Landau free energy [Eq. (1) in Ref. [13]], originally derived from the Ising model of ferromagnetic ordering of spins in the presence of dipole-dipole interactions [30,31], describes the key features of the nematic- SmZ_A -ferroelectric nematic phase sequence quite well. In the mixture case, two parameters, $\alpha(c)$ and $\beta(c)$, depend on the concentration c , where $\alpha(c)$ is the positive coefficient of $-\alpha(c)(dP_z/dy)^2$. This term drives the instability and the SmZ_A phase, which persists for all concentrations c until $\alpha(c)$ changes sign. Since pASC now demonstrates that SmZ_A persists all the way across the DIO-RM734 phase diagram, this model would say that $\alpha(c)$ goes to zero near 0% of DIO (i.e., pure RM734) or stays positive and small. The model is thus in agreement with the phase diagram of [15] and our new pASC results for pure RM734.

IV. CONCLUSIONS

Although in our previous work on RM734 we did not observe in our data a thermal signature for a possible N - N_x transition, we decided to make further efforts to improve the resolution and accuracy of the measurements and revisited the RM734 problem by focusing on the $c_p(T)$ profiles of various slow scans on samples from different batches. In this paper we presented new pASC results obtained for 20 scanning (heating and cooling) runs on five RM734 samples from four different batches as identified in Table I. The results of ten of these runs are displayed and discussed in Figs. 1–5. The results for the remaining runs are given in the associated Supplemental Material. From the analysis of all these results it is concluded

that also RM734 exhibits an intermediate N_x phase between the ferroelectric nematic N_F phase and the normal nematic phase N . For the temperature width of the N_x phase, a value of $\Delta T = 1.15 \pm 0.10$ K is obtained. For the N_x - N transition, a heat of transition $\Delta h = 0.0045 \pm 0.0005$ J/g was found. Combining these calorimetric results with other literature reports on thermodynamic and structural information in related systems, convincing evidence could be presented for the N_x phase of RM734 being the same as the N_x phase of DIO.

ACKNOWLEDGMENT

G.C. acknowledges the financial support of Project P1-0125 of the Slovene Research Agency.

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