Thermophysics of metal alkanoates
VI. Heat capacities and thermodynamic properties of lithium *n*-pentanoate and *n*-heptanoate [a]

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The adiabatic calorimetric study (at 5 to 350 K) of lithium *n*-pentanoate and *n*-heptanoate proved that solid-state transitions occur at $T_{trs}/K = 209.31$ and 319.06 in the former salt, and at $T_{trs}/K = 317.08$ in the latter one. Concerning *n*-pentanoate, the discontinuous (predominantly first-order) crystal-to-crystal transition at 209.31 K is followed almost immediately by a broad and diffused "hump" (with a maximum at 319.06 K), which stretches over a temperature range of about 110 K, and is apparently related to the occurrence of a gradual higher-order, possibly second-order) transformation. Concerning *n*-heptanoate, the nature and order of its single transition should be the same as suggested for the lower-temperature transformation of the shorter homolog. At the transition temperatures, the values of $C_{p,m}/R$, $\Delta_{trs}S_m/R$, and $\Delta_{trs}H_m/R$ are 27.4, 0.39, and 80 K; and 32.9, 1.94, and 330.1 K, for the 209.31 K and 319.06 K transitions of lithium *n*-pentanoate, respectively; and 7800, 2.228, and 702.44 K for lithium *n*-heptanoate. Thermodynamic functions are tabulated at selected temperatures for both samples.

1. Introduction

In the introduction to Paper V[1] of this series an analysis (based on previous d.s.c. results by one of us[2,3]) was made of the entropy changes involved in both the crystal-to-crystal transitions occurring at $T/K > 110$ (≈ 110 K being the lowest temperature accessible to d.s.c.), and the fusion processes of lithium *n*-alkanoates through eicosanoate ($n_C = 20$; n_C: number of carbon atoms).

Accordingly, it was asserted, *inter alia*, that homologs with $4 \leqslant n_C \leqslant 11$, and metastable propanoate, ought to exhibit related thermophysical behavior. It can now be further specified that discontinuous (first order)[4] phase changes would not be expected at $T/K < 110$ for either *n*-pentanoate or *n*-heptanoate (investigated in

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[a] The first paper in this series is reference 6.
† Died 24 January 1986.

the present paper) inasmuch as: (i) on the one hand, only the occurrence of a single inter-crystalline transformation in each of the latter salts would be compatible with the above assertion (see, e.g., figure 2 in reference 1); on the other hand, d.s.c. records have already provided evidence[2] for a transition at $T_{trs}/K = (201 \pm 2)$ in $CH_3(CH_2)_3CO_2Li$, and at $T_{trs}/K = (317.9 \pm 0.8)$ in $CH_3(CH_2)_5CO_2Li$. Unfortunately, no direct information is available on the structures of the phases involved, but it seems likely that they ought to be of the same lamellar type (double-layered arrangements of the alkali cations and polar ends of the anions; inter-layered tail-to-tail arrangements of the anionic hydrocarbon tails) whose existence was proved by Gallot and Skoulios[5] in even homologs with $n_C \geqslant 8$.

TABLE 1. Experimental heat capacities of lithium n-pentanoate and n-heptanoate $(R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
				Lithium n-pentanoate					
Series I		319.05	32.887	204.70	18.192	173.48	13.613	8.27	0.058
174.35	13.684	320.05	32.884	206.73	22.703	179.59	14.012	8.88	0.071
180.08	14.071	321.05	32.798	208.24	24.478	185.71	14.372	9.48	0.091
185.38	14.379	322.04	33.436	209.31	25.224	191.83	14.733	10.08	0.106
190.71	14.711	323.04	32.609	210.40	23.922	Series VIII		10.69	0.127
197.44	15.258	325.04	32.683	211.53	22.732	58.53	5.139	11.32	0.146
204.77	22.268	326.34	31.921	212.70	21.942	64.10	5.727	11.95	0.173
210.77	28.598	327.93	31.377	214.45	20.250	68.78	6.177	12.57	0.198
217.08	20.441	329.94	30.652	216.74	18.639	73.57	6.612	13.20	0.231
224.48	18.111	332.37	29.839	219.00	17.966	78.41	7.050	13.84	0.261
232.17	17.958	336.54	28.601	221.21	17.648	83.28	7.499	14.61	0.306
239.69	18.391	342.42	27.418	223.40	17.528	88.17	7.919	15.49	0.365
246.71	19.057	345.86	26.965	226.05	17.620	93.11	8.295	16.37	0.426
253.49	19.722	346.89	27.222	232.67	17.936	98.09	8.664	17.27	0.492
260.12	20.443	347.93	26.860	236.78	18.134	103.07	9.033	18.17	0.564
266.82	21.230	348.98	26.895	Series VI		108.06	9.393	19.29	0.659
273.48	22.124	Series III		ΔH_m detn. C		113.08	9.752	20.61	0.777
280.14	23.166	280.97	23.296	$\Delta_{trs} H_m$ detn. C		Series IX		21.93	0.908
286.77	24.370	ΔH_m detn. A		225.38	17.452	7.51	0.037	23.26	1.043
293.37	25.725	$\Delta_{trs} H_m$ detn. A		Series VII		7.98	0.051	24.61	1.186
299.95	27.393	337.01	28.537	104.27	9.120	8.42	0.065	25.98	1.335
306.50	29.390	338.08	28.462	110.09	9.546	8.95	0.074	27.65	1.527
313.04	31.387	Series IV		115.10	9.885	9.48	0.092	29.62	1.756
319.65	32.693	300.02	27.423	120.13	10.242	10.02	0.101	31.59	1.990
326.50	31.750	$\Delta_{trs} H_m$ detn. B		125.18	10.595	10.56	0.124	33.59	2.239
333.63	29.387	336.26	28.539	130.24	10.936	11.09	0.138	35.60	2.487
Series II		Series V		135.31	11.253	11.65	0.156	38.16	2.802
292.62	25.488	ΔH_m detn. B		140.38	11.588	12.19	0.185	41.23	3.172
299.38	27.239	194.56	15.005	145.47	11.912	12.74	0.204	44.31	3.542
307.59	29.679	197.61	15.245	150.56	12.222	13.46	0.241	47.44	3.907
313.49	31.621	200.28	15.517	155.65	12.552	Series X		50.61	4.273
315.51	32.166	202.54	16.071	161.26	12.888	7.74	0.050	54.13	4.661
317.04	32.676			167.37	13.243			57.99	5.072
318.05	32.782							61.87	5.490

TABLE 1—continued

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
				Lithium n-heptanoate					
Series I		135.47	14.119	12.22	0.230	Series V		Series VII	
207.70	19.360	141.53	14.578	13.16	0.286	67.61	7.647	261.14	23.546
214.04	19.802	147.61	15.034	14.16	0.356	71.71	8.175	263.70	23.771
220.18	20.251	153.70	15.493	15.17	0.439	76.07	8.680	273.40	24.787
226.33	20.720	160.05	15.965	16.19	0.525	81.17	9.281	ΔH_m detn. F	
232.48	21.198	166.66	16.426	17.24	0.621	86.99	9.921	$\Delta_{trs}H_m$ detn. A	
238.63	21.674	173.27	16.916	18.30	0.727	92.85	10.479		
244.78	22.174	179.89	17.350	19.37	0.846			Series VIII	
250.92	22.685	186.52	17.841	20.45	0.965	Series VI		226.12	20.694
257.07	23.178	193.66	18.325	21.55	1.102	ΔH_m detn. B		ΔH_m detn. G	
263.21	23.749	201.30	18.857	22.65	1.244	ΔH_m detn. C		ΔH_m detn. H	
269.36	24.314	208.95	19.409	23.76	1.363	ΔH_m detn. D		310.49	29.933
275.75	24.973	216.59	19.977	24.87	1.542	ΔH_m detn. E		$\Delta_{trs}H_m$ detn. B	
282.39	25.682			26.74	1.802	301.59	28.132	326.73	41.799
289.02	26.420	Series III		29.31	2.183	308.87	29.406	328.81	41.456
295.65	27.217	9.96	0.14	31.87	2.572	314.29	32.241		
302.50	28.276	11.32	0.180	34.48	2.982	316.41	119.31	Series IX	
309.59	29.538	12.08	0.218	37.39	3.436	316.79	443.16	262.72	23.685
		12.96	0.274	40.58	3.927	316.89	661.10	ΔH_m detn. I	
Series II		13.84	0.331	43.81	4.422	316.96	653.4	ΔH_m detn. J	
92.91	10.483	14.81	0.405	47.09	4.907	317.01	905.0	$\Delta_{trs}H_m$ detn. C	
99.47	11.084	15.85	0.494	50.42	5.394	317.08	1071	324.58	43.452
105.40	11.591	16.91	0.586	53.79	5.878	317.17	850.7	327.77	41.631
111.37	12.128	17.97	0.695	57.19	6.347	317.28	640.9	336.35	39.667
117.37	12.629	Series IV		ΔH_m detn. A		317.57	244.76	343.86	37.988
123.38	13.167	10.86	0.16	74.30	8.496	318.61	57.416		
129.42	13.671			90.04	10.209	320.43	43.421		

Gallot and Skoulios's statement, formulated for the even homologs they submitted to X-ray diffractometric analysis, that (for a given type of solid-to-solid transition) the longer the tail is, the higher T_{trs} must be (as a consequence of the fact that increasing tail lengths increasingly hamper the re-arrangement of the tails subsequent to the re-arrangement of the polar end groups due to the structural transformation)[5] is still valid for the series of the odd homologs (and, in particular, for n-pentanoate and n-heptanoate) when considered separately. It can be added that, according to Skoda,[4] a methyl end group packing differently in the odd and even homologs could be the cause of the alternation effect observed in the alkali alkanoates for a number of physicochemical properties. The inter-crystalline transition temperatures of lithium n-alkanoates discussed in reference 1 are to be listed among these, and it is peculiar that this alternation effect eventually tends toward elimination of inter-crystalline discontinuous transitions in short-chain even-numbered homologs.

Until now, $C_{p,m}$s have been completely missing for either lithium n-pentanoate or n-heptanoate, and information on the entropy changes involved in phase transformations is restricted to the d.s.c. results reported in reference 2.

2. Experimental

The salts were obtained by reaction of Fluka puriss ($\geqslant 99.5$ moles per cent) Li_2CO_3 suspended in anhydrous methanol with Fluka puriss n-pentanoic (> 99.5) and n-heptanoic (> 99) acid, respectively. The purification procedure was similar to that adopted for n-butanoate and n-hexanoate, and detailed in reference 1. The equilibrium calorimetric measurements were performed in the Mark X cryostat, using the gold-plated copper calorimeter designated W–62, and the automated computerization system already described in reference 6.

The lithium n-pentanoate and n-heptanoate samples loaded in the calorimeter had masses 21.815 g ($\hat{=} 0.20187$ mol on the basis of the 1973 IUPAC atomic masses), and 18.668 g ($\hat{=} 0.13715$ mol), respectively.

The buoyancy corrections were calculated using for n-pentanoate the density (1.15 ± 0.02) g·cm^{-3} measured by Spinolo[7] by the density-bottle method, and for n-heptanoate the density 1.11 g·cm^{-3} obtained by interpolation of Spinolo's results for n-butanoate, n-pentanoate, and n-hexanoate, and Gallot and Skoulios's findings[5] on higher homologs.

3. Results

HEAT CAPACITIES AND DERIVED FUNCTIONS

The experimental heat capacities (listed in chronological order) are reported as ratios $C_{p,m}/R$ in table 1, and plotted in figures 1 and 2 for n-pentanoate and n-heptanoate, respectively. Apart from the transition regions, the numerical results have been fitted to appropriate orthogonal polynomials, on the basis of which the relevant thermodynamic functions (as well as smoothed $C_{p,m}/R$ values) were calculated for selected temperatures (table 2). Within the transition regions, a procedure similar to that described, *e.g.* in reference 8, was adopted to separate the lattice contributions from the overall enthalpy and entropy increments.

LITHIUM n-PENTANOATE

The d.s.c. traces recorded[2] in 1977 on the n-pentanoate sample henceforth denoted as "1977–S" provided evidence for the occurrence of a single solid-state transformation at (201 ± 2) K. The "1984–S" salt employed for the present investigation, when submitted to d.s.c. analysis, proved to melt at the same temperature (576 to 577 K) as "1977–S" (although exhibiting a sharper and more symmetrical fusion peak), but to undergo the solid-state transition at a somewhat higher T_{trs} value (*i.e.* 206 to 207 K). Indeed, a critical re-examination of the purification procedure of "1977–S" led to the conclusion that this sample could have been contaminated by the presence of some unreacted lithium carbonate. Records taken on a new "1985–S" sample agreed fairly with those taken on "1984–S".

TABLE 2. Molar thermodynamic functions of lithium n-pentanoate and n-heptanoate

$$\{R = 8.3144 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1};\ \Phi^{\circ}_{\text{m}}(T, 0) \overset{\text{def}}{=} -\Delta_0^T H^{\circ}_{\text{m}}(T)/T + \Delta_0^T S^{\circ}_{\text{m}}(T)\}$$

$\dfrac{T}{K}$	$\dfrac{C_{p,\text{m}}}{R}$	$\dfrac{\Delta_0^T S^{\circ}_{\text{m}}}{R}$	$\dfrac{\Delta_0^T H^{\circ}_{\text{m}}}{R\cdot K}$	$\dfrac{\Phi^{\circ}_{\text{m}}(T, 0)}{RT}$	$\dfrac{T}{K}$	$\dfrac{C_{p,\text{m}}}{R}$	$\dfrac{\Delta_0^T S^{\circ}_{\text{m}}}{R}$	$\dfrac{\Delta_0^T H^{\circ}_{\text{m}}}{R\cdot K}$	$\dfrac{\Phi^{\circ}_{\text{m}}(T, 0)}{RT}$
				Lithium n-pentanoate					
				Phase II					
0	0	0	0	0	80	7.208	4.892	249.66	1.771
5	0.013	0.004	0.016	0.001	90	8.045	5.790	325.99	2.168
10	0.103	0.035	0.264	0.009	100	8.813	6.678	410.33	2.575
15	0.331	0.114	1.277	0.029	120	10.231	8.412	600.9	3.404
20	0.723	0.260	3.853	0.067	140	11.567	10.090	819.1	4.240
30	1.801	0.747	16.245	0.206	160	12.803	11.716	1062.9	5.073
40	3.026	1.433	40.370	0.424	180	14.036	13.295	1331.2	5.900
50	4.202	2.235	76.56	0.704	200 [a]	(15.49)	(14.84)	(1625.2)	(6.72)
60	5.292	3.099	124.11	1.031		[15.49]	[14.84]	[1625.2]	[6.72]
70	6.291	3.991	182.10	1.390	209.31 [b] (≈27.40)		(15.56)	(1772.0)	(7.09)
						[16.10]	[15.56]	[1772.0]	[7.09]
				Phase I					
209.31 [b] (≈27.40)		(15.95)	(1854.51)	(7.09)	260	20.43	19.86	2768.79	9.21
	[16.10]	[15.56]	[1772.0]	[7.09]	280	23.15	21.46	3200.52	10.03
230	17.7	(17.54)	(2200.90)	(7.97)	298.15	26.95	23.88	3652.02	11.63
	[17.7]	[17.15]	[2121.47]	[7.93]	300	27.45	24.05	3702.27	11.71
235	18.04	17.93	2290.13	8.18	350	≈26.9	28.66	5191.63	13.83
240	18.40	18.31	2381.24	8.39		[26.9]	[26.72] [c]	[4862.73] [c]	[12.83]
				Lithium n-heptanoate					
				Phase II					
0	0	0	0	0	180	17.37	16.76	1672.5	7.466
5	0.017	0.006	0.021	0.002	200	18.78	18.66	2033.9	8.491
10	0.127	0.042	0.318	0.010	220	20.24	20.52	2424.0	9.500
15	0.420	0.141	1.594	0.035	240	21.78	22.34	2844.0	10.494
20	0.918	0.326	4.865	0.083	260	23.46	24.15	3296.0	11.475
30	2.286	0.945	20.589	0.259	280	25.41	25.96	3784.1	12.445
40	3.840	1.815	51.21	0.535	300	27.87	27.79	4315.7	13.407
50	5.334	2.834	97.15	0.891	305 [a]	28.67	(28.26)	(4457.0)	(13.65)
60	6.725	3.932	157.55	1.306		[28.67]	[28.26]	[4457.0]	[13.65]
70	8.000	5.065	231.27	1.762	310	29.64	(28.73)	(4602.7)	(13.88)
80	9.152	6.210	317.13	2.246		[29.44]	[28.73]	[4602.3]	[13.88]
90	10.192	7.349	413.94	2.750	315	33.00	(29.21)	(4751.4)	(14.13)
100	11.142	8.473	520.7	3.266		[30.22]	[29.21]	[4751.4]	[14.13]
120	12.872	10.660	761.1	4.317	317.08 [b]	(≈7800)	(29.41)	(4814.7)	(14.23)
140	14.469	12.766	1034.7	5.375		[30.56]	[29.41]	[4814.7]	[14.23]
160	15.96	14.796	1339.1	6.426					
				Phase I					
317.08 [b]	(≈7800)	(31.64)	(5520.36)	(14.23)		[42.11]	[30.47]	[5153.7]	[14.61]
	[43.51]	[29.41]	[4814.7]	[14.23]	330	41.14	33.34	6063.6	14.97
320	43.40	(32.04)	(5642.4)	(14.41)	340	38.86	35.17	6672.1	15.55
	[42.99]	[29.81]	[4940.9]	[14.37]	350	36.55	38.09	7657.6	16.21
325	42.11	(32.70)	(5855.2)	(14.68)					

[a] Quantities in parentheses represent either estimated heat capacities or thermodynamic functions on the arbitrary assumption that the transitions are truly isothermal at the transition temperature indicated.

[b] Quantities in square brackets represent selected lattice heat capacities or the integrated thermodynamic functions of the selected lattice.

[c] These are obtained by integration of a representative lattice line of the heat capacity from 240 K to 350 K and adding to the value at 240 K.
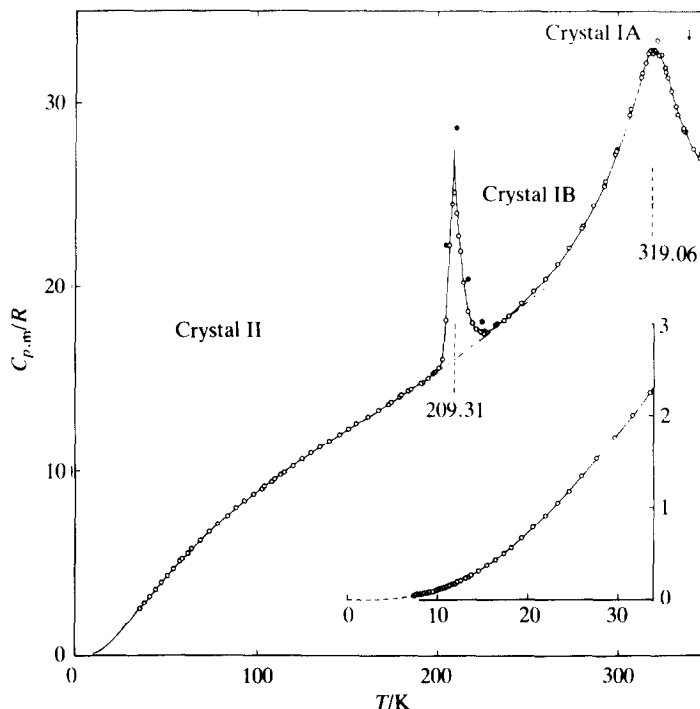
FIGURE 1. Heat capacities of lithium n-pentanoate taken in the Mark X cryostat below 350 K. The interval 0 to 34 K is magnified in the lower-right part of the figure. For explanation of symbols, see text.

The latter sample was submitted in the Mark X cryostat to the thermal cycles:

(1) $300 \text{ K} \xrightarrow{48 \text{ h}} 170 \text{ K} \xrightarrow{11.5 \text{ h, Series I}} 337 \text{ K,}$

(2) $337 \text{ K} \xrightarrow{35 \text{ h}} 238 \text{ K} \xrightarrow{14 \text{ h, Series II}} 349.5 \text{ K,}$

(3) $349.5 \text{ K} \xrightarrow{9 \text{ h}} 279 \text{ K} \xrightarrow{7 \text{ h, Series III}} 339 \text{ K,}$

(4) $339 \text{ K} \xrightarrow{2 \text{ h}} 300 \text{ K} \xrightarrow{2.25 \text{ h, Series IV}} 337 \text{ K,}$

(5) $337 \text{ K} \xrightarrow{19 \text{ h}} 173 \text{ K} \xrightarrow{8.5 \text{ h, Series V}} 239 \text{ K,}$

(6) $239 \text{ K} \xrightarrow{13 \text{ h}} 172 \text{ K} \xrightarrow{2.5 \text{ h, Series VI}} 225 \text{ K,}$

(7) $225 \text{ K} \xrightarrow{50 \text{ h}} 100 \text{ K} \xrightarrow{7 \text{ h, Series VII}} 195 \text{ K,}$

(8) $195 \text{ K} \xrightarrow{12.5 \text{ h}} 54 \text{ K} \xrightarrow{5 \text{ h, Series VIII}} 116 \text{ K,}$

(9) $116 \text{ K} \xrightarrow{50 \text{ h}} 6 \text{ K} \xrightarrow{3.5 \text{ h, Series IX}} 14 \text{ K,}$

(10) $14 \text{ K} \xrightarrow{0.5 \text{ h}} 6 \text{ K} \xrightarrow{9 \text{ h, Series X}} 64 \text{ K.}$
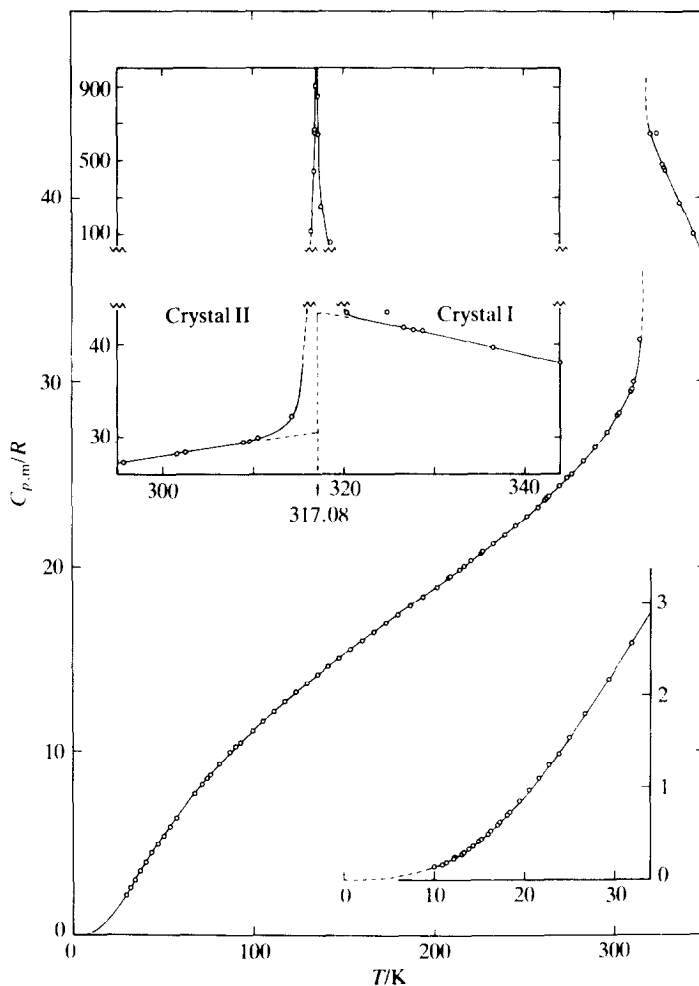
FIGURE 2. Heat capacities of lithium *n*-hepatonoate taken in the Mark X cryostat below 350 K. The intervals 295 to 344 K (which includes the II → I transition region) and 0 to 34 K are magnified in the upper-left and in the lower-right parts of the figure, respectively.

Series I to IV showed that the transition expected a little above 200 K was soon followed by an unexpected broad and diffuse "hump", stretching over a temperature range of about 110 K, and characterized by the presence of a maximum at 319.06 K. The existence of this hump escaped previous d.s.c. investigation due to its breadth, and to the low (*i.e.* ≤0.17 K·s⁻¹) scanning rates usually employed. D.s.c. evidence for it, however, could be obtained subsequently for all the "1977-S", "1984-S", and "1985-S" *n*-pentanoates from the traces recorded on samples run (in a single step) from 180 to 350 K at a scan speed ≥ 0.33 K·s⁻¹.

In conclusion, the sequence of phases suggested in reference 2 for lithium

n-pentanoate, *i.e.*

$$\text{Crystal II} \rightleftarrows \text{Crystal I} \rightleftarrows \text{Isotropic liquid,}$$

must be modified as follows:

$$\text{Crystal II} \xrightleftharpoons[\substack{(206 \text{ to } 207) \text{ K by d.s.c.} \\ 209.31 \text{ K by ad. cal. (see below)}}]{T_{\text{II}\rightarrow\text{IB}}} \text{Crystal IB} \xrightleftharpoons[319.06 \text{ K by ad. cal.}]{T_{\text{IB}\rightarrow\text{IA}}}$$

$$\text{Crystal IA} \xrightleftharpoons[(576 \text{ to } 577) \text{ K by d.s.c.}]{T_{\text{fus}}} \text{Isotropic liquid.}$$
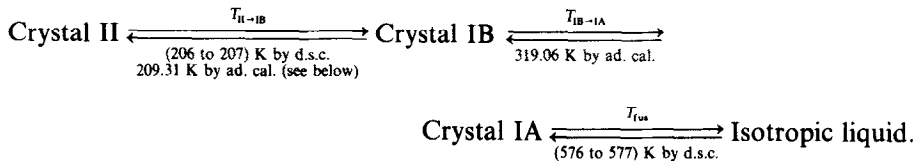
LITHIUM n-HEPTANOATE

D.s.c. provided evidence[2] for the phase relations:

$$\text{Crystal II} \xrightleftharpoons[(317.9 \pm 0.8) \text{ K}]{T_{\text{II}\rightarrow\text{I}}} \text{Crystal I} \xrightleftharpoons[(550 \pm 1) \text{ K}]{T_{\text{fus}}} \text{Isotropic liquid,}$$
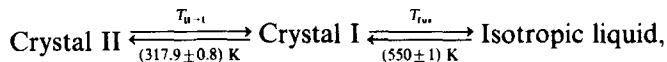
the absence of any mesomorphic phase being coherent, *inter alia*, with the trend of the clearing entropy changes of the other alkali n-heptanoates (each of which can exist in the liquid crystalline state) when plotted against the cationic radius; indeed, the interpolating parabola $\Delta_{\text{clr}}S_{\text{m}}/R = \{-0.610 + 1.049 \times 10^{-2}(r_+/\text{pm}) - 0.117 \times 10^{-4}(r_+/\text{pm})^2\}$ (Curve A in figure 3) cuts the abscissa at $r_+/\text{pm} > 60$, the ionic radius of Li$^+$ being 60 pm.[9]
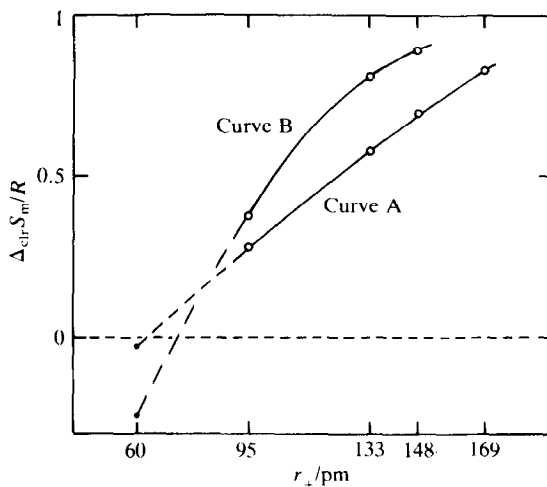
FIGURE 3. The $\Delta_{\text{clr}}S_{\text{m}}/R$ values[2] for Ns, K, Rb, and Cs n-heptanoates as a function of the cationic radius (curve A); $r_+/\text{pm} = 60$, 95, 133, 148, and 169 for Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$. respectively.[9] For comparison, the analogous values reported in reference 2 for the n-pentanoates of Na, K, and Rb are also shown (curve B).

The sample investigated here was submitted in the cryostat to the thermal cycles:

(1) $305 \text{ K} \xrightarrow{12 \text{ h}} 204 \text{ K} \xrightarrow{11.5 \text{ h, Series I}} 313 \text{ K}$,

(2) $313 \text{ K} \xrightarrow{16 \text{ h}} 82 \text{ K} \xrightarrow{9.5 \text{ h, Series II}} 220 \text{ K}$,

(3) $220 \text{ K} \xrightarrow{10 \text{ h}} 6 \text{ K} \xrightarrow{3.5 \text{ h, Series III}} 18.5 \text{ K}$,

(4) $18.5 \text{ K} \xrightarrow{0.5 \text{ h}} 9 \text{ K} \xrightarrow{9 \text{ h, Series IV}} 94 \text{ K}$,

(5) $94 \text{ K} \xrightarrow{1.5 \text{ h}} 65 \text{ K} \xrightarrow{3 \text{ h, Series V}} 95 \text{ K}$,

(6) $95 \text{ K} \xrightarrow{20 \text{ h}} 58.5 \text{ K} \xrightarrow{14 \text{ h, Series VI}} 320 \text{ K}$,

(7) $320 \text{ K} \xrightarrow{10 \text{ h}} 260 \text{ K} \xrightarrow{6 \text{ h, Series VII}} 348 \text{ K}$,

(8) $348 \text{ K} \xrightarrow{20 \text{ h}} 224 \text{ K} \xrightarrow{4.5 \text{ h, Series VIII}} 330 \text{ K}$,

(9) $330 \text{ K} \xrightarrow{43 \text{ h}} 182 \text{ K} \xrightarrow{6.5 \text{ h, Series IX}} 326 \text{ K}$.

The salt underwent transformations from crystal II to crystal I in cycles (6) to (9), and from crystal I to crystal II in cycles (7) to (9). During the latter, the temperatures of deepest cooling were 260, 224, and 182 K, respectively, d.s.c. having already proved that cooling crystal I to room temperature was sufficient to obtain complete conversion to crystal II.

4. Discussion

The temperature at which the (apparent) $C_{p,\text{m}}/R$ goes through a maximum were taken as the (adiabatic calorimetric) transition temperatures.

For the single transition of lithium n-heptanoate, the value $T_{\text{trs}}/\text{K} = 317.08$ can be drawn from table 1, Series VI. The previous d.s.c. value, $T_{\text{trs}}/\text{K} = (317.9 \pm 0.8)$,[10]

TABLE 3. Enthalpy and entropy of 317.08 K transition in lithium n-heptanoate
($R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

Designation	No. of detns.	$\dfrac{T_1}{\text{K}}$	$\dfrac{T_2}{\text{K}}$	$\dfrac{\Delta_{T_1}^{T_2} H_\text{m}}{R \cdot \text{K}}$	$\dfrac{\Delta_{305 \text{ K}}^{325 \text{ K}} H_\text{m}}{R \cdot \text{K}}$	$\dfrac{\Delta_{305 \text{ K}}^{325 \text{ K}} S_\text{m}}{R}$
		II → I Transition (317.08 K)				
Series V	13	305.24	321.45	1245.12	1395.93	
Series VI	1	310.27	322.95	1159.98	1399.89	
Series VII	1	312.94	325.69	1195.59	1400.95	
Series VIII	1	310.32	323.57	1180.90	1395.94	
Graphical integration					1402.98	4.433
				mean:	1399.14 ± 2.6	
Lattice contribution					696.70	2.206
				$\Delta_{\text{trs}} H_\text{m}/(R \cdot \text{K})$:	702.44 ± 2.6	
				$\Delta_{\text{trs}} S_\text{m}/R$:		2.228

TABLE 4. Enthalpy and entropy of 209.31 K transition in lithium n-pentanoate
$(R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$

Designation	No. of detns.	$\dfrac{T_1}{\text{K}}$	$\dfrac{T_2}{\text{K}}$	$\dfrac{\Delta_{T_1}^{T_2} H_m}{R \cdot \text{K}}$	$\dfrac{\Delta_{200\,\text{K}}^{230\,\text{K}} H_m}{R \cdot \text{K}}$	$\dfrac{\Delta_{200\,\text{K}}^{230\,\text{K}} S_m}{R}$
Series I	6	193.37	236.02	850.54	642.1 [a]	
Series V	15	199.15	227.61	551.85	580.9	
Series VI	2	192.86	225.91	606.39	570.2	
Graphical integration					579.3	2.70
				mean:	576 ± 4	
Lattice contribution (estimated)					496	2.31
				$\Delta_{trs} H_m/(R \cdot \text{K})$:	80 ± 4	
				$\Delta_{trs} S_m/R$:		0.39

[a] Not included in average.

fully coincides with the new one. Details on the results obtained for the enthalpy and entropy change associated with the transition are reported in table 3. Again, the previous d.s.c. findings, $\Delta_{trs} H_m/R = (684 \pm 10)$ K and $\Delta_{trs} S_m/R = (2.15 \pm 0.04)$,[10] compare favorably with the present results obtained at thermodynamic equilibrium: (702.4 ± 2.6) K and 2.228, respectively.

Concerning the transition order, it can be observed that: (i) a true lattice transformation is probably involved in the transition (as noted in the Introduction), although it possibly consists of a mere variation of the tilt angles; (ii) the (apparent) $C_{p,m}/R$ value (1071; see table 1, Series VI) measured at T_{trs} is at least 35 and 24 times larger than the lattice heat capacities of crystal II and crystal I, respectively, at the same temperature, $i.e.$ the transition "peak" is remarkably sharp; and (iii) deviations of the (apparent) $C_{p,m}/R$ values from the interpolating polynomials, however, are observed between about 305 and about 325 K (see table 2); consequently, the transition is positively not to be considered as isothermal.

Hence, it seems reasonable to assume that the transition II-to-I is predominantly first order, although occurring somewhat gradually. A similar situation was already

TABLE 5. Enthalpy and entropy of transformation at 319.06 K in lithium n-pentanoate
$(R = 8.3144 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$

Designation	No. of detns.	$\dfrac{T_1}{\text{K}}$	$\dfrac{T_2}{\text{K}}$	$\dfrac{\Delta_{T_1}^{T_2} H_m}{R \cdot \text{K}}$	$\dfrac{\Delta_{240\,\text{K}}^{350\,\text{K}} H_m}{R \cdot \text{K}}$	$\dfrac{\Delta_{240\,\text{K}}^{350\,\text{K}} S_m}{R}$
Series I	15	236.02	337.25	2536.60	2811.6	
Series II	23	296.06	349.49	1584.59	2814.5	
Series III	1	301.51	336.46	1074.01	2808.6	
Series IV	1	300.77	335.71	1072.47	2807.9	
Graphical integration					2812.7	10.35
				mean:	2811.1 ± 1.5	
Lattice contribution (estimated)					2481.0	8.41
				$\Delta_{trs} H_m/(R \cdot \text{K})$:	330.1 ± 1.5	
				$\Delta_{trs} S_m/R$:		1.94

met[8] and discussed for the transition III-to-II of potassium propanoate ($T_{trs}/K = 255 \pm 1$); here the temperature range over which the phase transformation occurred (about 60 K) was approximately three times larger than in the present case.

At $T > T_{trs}$ there is a linear and descending trend of the $C_{p,m}/R$ plot which makes it difficult to predict with certainty the direction of the $C_{p,m}/R$ curve after 350 K but when higher-temperature values are obtained by superambient calorimetry and/or d.s.c. it will be possible to complete the $C_{p,m}/R$ curve for this sample.

The lower-temperature transformation of lithium n-pentanoate appears similar to that of the n-heptanoate single transition. The following points, however, are to be stressed. (i) Poorer than usual reproducibility exists in the transition region between the results of Series I {6 experimental points (● in figure 2); see table 4}, and Series V (15 experimental points). Though the reasons for this are not fully understood, more reliability is attached to Series V, due to the larger number of experimental points, and the satisfactory agreement existing between the $\Delta_{trs}H_m/R$ values obtained from this series, on the one hand, and from Series VI and graphical integration, on the other hand (see table 4). (ii) Accordingly, 209.31 K (*i.e.* the temperature at which the apparent $C_{p,m}/R$ of Series V goes through a maximum) is suggested as the adiabatic-calorimetric T_{trs} value: previous d.s.c. figures have already been discussed. (iii) The designation of this transition as discontinuous and predominantly first order is coherent with both the morphology of the peak and the general statements made in Paper V of the present series.[1]

Details on the higher-temperature transformation of n-pentanoate are collected in table 5. It is also apparent from an inspection of figure 2 that this transition occurs very gradually, thus allowing one to assume reasonably that this is of higher (possibly second; see below) order, and accordingly to be related to some kind of intramolecular orientational variation. This assumption might be supported by two observations (quoted here) by Skoda,[4] who studied dilatometrically the phase transitions of the even and odd lithium n-alkanoates from n-tetradecanoate ($n_C = 14$) to n-octadecanoate ($n_C = 18$).

(i) "In their crystalline forms, at room temperature $\cdots$ a closer molecular packing is attained in the odd $\cdots$ lithium soaps, whereas this is the case with the even soaps in the structures occurring above ca. 120 °C."[4] Extension to lower homologs allows one to assume that lithium n-pentanoate crystal II (stable at $T < 209$ K) ought to exhibit a closer molecular packing than crystal I.

TABLE 6. Comparison of lithium n-pentanoate enthalpy-type determinations with integrated smooth-curve heat capacities ($R = 8.314$ J $\cdot$ K$^{-1} \cdot$ mol^{-1})

Designation	$\dfrac{T_1}{K}$	$\dfrac{T_2}{K}$	$\dfrac{\Delta H_m}{R \cdot K}$	$\dfrac{\int C_{p,m}\,dT}{R \cdot K}$	$10^2\Delta^a$
A	282.01	301.50	495.59	496.59	0.20
B	173.94	193.05	273.82	272.80	0.37
C	173.73	192.87	273.54	272.94	0.22

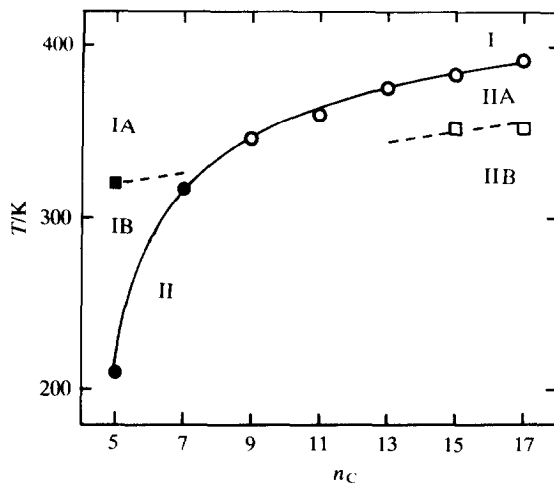^{a} $\Delta = |(\text{Column 3} - \text{Column 4})|/\text{Column 4}$.

FIGURE 4. Solid-to-solid transformations in odd lithium n-alkanoates. Discontinuous (predominantly first-order) transitions detected: ●, by adiabatic calorimetry (this work); and ○, by d.s.c.;[3,10] gradual (higher order, possibly second-order) transitions detected: ■, by adiabatic calorimetry (this work); and □, by dilatometry.[4]

(ii) "··· the lithium soaps show ··· three distinct transition regions: at about 110 °C a polymorphic transition occurs between the two crystalline modifications, at about 200 °C the soaps pass into a mesomorphic phase ('Ribbon'-structure), and at about 230 °C into the molten state.† Besides these first-order transitions, a second-order transition in the solid state at about 80 °C in both the even and odd members was observed".[4]‡ Extension to lower homologs might cause, at first sight, the gradual (higher-order, possibly second-order) transition in lithium n-pentanoate at 319 K to appear coherent with the occurrence of similar transitions in Skoda's soaps at about 353 K, as the T_{trs} values relevant to a given set of trans-formations tend to decrease with decreasing n_C. But in lithium n-tetradecanoate through n-octadecanoate these transitions occur at a temperature (about 353 K)[4] lower than that (about 383 K)[4] of the discontinuous transition, whereas for lithium n-pentanoate the contrary occurs. This, however, might be justified on the basis of Skoda's first observation. Indeed, long hydrocarbon tails are less rigidly held by the electrostatic sandwich than short tails. Consequently, orientational variations might occur in long-chain homologs, at adequate temperatures, even in the closer molecular packing (i.e. in crystal II for odd n_C values), whereas these variations might occur in short-chain homologs only after transformation into the less close molecular packing (i.e. in crystal I for odd n_C values).

† Until here, d.s.c. results[3] on long-chain lithium n-alkanoates are perfectly coherent with Skoda's picture.
‡ This type of transition in long-chain lithium n-alkanoates escaped both d.s.c. investigation,[3] and Gallot and Skoulios's X-ray diffractometric analysis.[5] However, taking into account the present (adiabatic-calorimetric and d.s.c.) findings on n-pentanoate, it seems now possible that d.s.c. evidence might have been obtained from traces recorded at scanning rates higher than those employed in reference 3. This point will be ascertained in the future.

TABLE 7. Comparison of lithium n-heptanoate enthalpy-type determinations with integrated smooth-curve capacities ($R = 8.1344$ J·K^{-1}·mol^{-1})

Designation	$\dfrac{T_1}{K}$	$\dfrac{T_2}{K}$	$\dfrac{\Delta H_m}{R \cdot K}$	$\dfrac{\int C_{p,m}\,dT}{R \cdot K}$	$10^2 \Delta$ [a]
A	58.90	70.55	85.62	85.37	0.28
B	120.04	158.40	552.16	553.16	0.18
C	158.42	202.95	776.85	775.91	0.12
D	202.95	250.14	981.33	980.11	0.12
E	250.14	297.95	1194.87	1191.64	0.27
F	281.53	310.27	788.62	788.82	0.03
G	227.15	275.32	1095.85	1096.52	0.06
H	275.32	305.32	801.37	801.57	0.02
I	263.75	281.53	438.66	439.00	0.08
J	281.53	310.32	790.53	790.37	0.02

[a] $\Delta = |(\text{Column 3} - \text{Column 4})|/(\text{Column 4})$.

For lithium n-heptanoate, it might be expected (see figure 4) that the gradual transition occurs at a temperature still higher than, but close to, that of the discontinuous transition. Actually, the former transformation being diffused, the two transitions should almost overlap; this might represent a possible explanation of the descending trend of the $C_{p,m}/R$ values observed at 325 to 350 K for the n-heptanoate.

Finally, it is worth mentioning that a test of the precision of the overall calorimetric procedure (particularly important for the transition regions) is obtained by comparing the results provided by the $C_{p,m}$-type runs with several ΔH_m-type determinations (see tables 6 and 7 for n-pentanoate and n-heptanoate, respectively): very satisfactory agreement is usually obtained.

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